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Nuclear Magnetic Resonance (nmr) Studies Of Germanium-73, Titanium-47,49,niobium-93 And Antimony-121

Harry Garth Spinney

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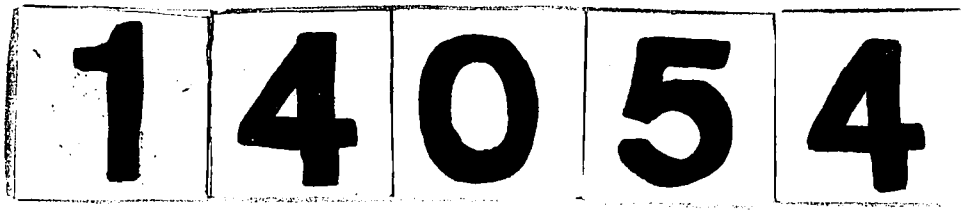

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NUCLEAR MAGNETIC RESONANCE STUDIES OF ^{73}Ge, $^{47,49}Ti$, ^{93}Nb and ^{121}Sb

by

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ABSTRACT

Nuclear magnetic resonance (nmr) solution studies of $^{73}Ge(IV)$, $^{47,49}Ti(IV)$, $^{121}Sb(V)$ and $^{93}Nb(V)$ in tetrahedral halogen (Ge and Ti) and octahedral halogen (Nb and Sb), pseudo-halogen (Nb) and halogen-adduct (Nb) environments are herein presented. A variety of ligand redistribution reactions are examined by nmr techniques, resulting in an extensive collection of chemical shift data representative of the natures of such redistribution species.

Empirical aids are applied to assist in the interpretation of this chemical shift data; however, by far the most successful of these approaches is the current extension of the Pairwise Additivity concept to the octahedral case, which has resulted in a powerful technique for identifying in solution the presence of specific geometric isomers. The direct consequence of this is the successful interpretation of several complex systems in labile equilibria where in all probability, other methods would have failed. The revealed ambidentate nature of thiocyanate ion in niobium-chloride acetonitrile solutions illustrates this claim.

The pairwise interaction parameter values generated by application of the Pairwise Additivity model to observed shifts, in addition to permitting structural identifications in solution and calculation of shifts of as yet unobserved species, are found to be transferable between neutral and anionic species of the same metal in a similar solvent and coordination arrangement.

An anomalous order of nuclear shielding is observed for the d^0 metals, Ti and Nb. This anomaly could not be satisfactorily accounted for on the basis of the established theoretical model describing the chemical shift, although the periodic applicability of the empirical model is not affected.

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CHAPTER I

INTRODUCTION

Nuclear Magnetic Resonance (nmr) is one of the outstanding discoveries of the twentieth century. The development of nmr spectroscopy has been dominated by the study of the hydrogen nucleus (^{1}H), although recent years have seen more emphasis placed on study of ^{19}F, ^{31}P, ^{14}N and especially Fourier Transform techniques as applied to ^{13}C. Studies of several of the many 'less-sensitive' heavy nuclei have been reported, although too few in number to allow establishment of any general periodic patterns of nmr spectral parameters.

The intent of this study has been to establish nmr spectral parameters for chemical systems of several well-known 'less-sensitive' nuclei, namely $^{47,49}Ti(IV)$, $^{73}Ge(IV)$, $^{93}Nb(V)$ and $^{121}Sb(V)$. (These particular nuclei have been little studied by nmr.) In this study, the chemical shift parameter has proved to be a most valuable and versatile probe into certain chemical systems normally difficult or impossible to examine through other techniques.

Chemical shift data for tetrahedral halide species

of the Group IVA and IVB elements, titanium and germanium, were obtained. Rapid chemical exchange was observed among mixed halo-species of Ti(IV); however, exchange rates of the mixed halo-species of Ge(IV) were sufficiently slow such that chemical shift data were obtained for all possible species. This latter chemical shift data set demonstrated a second-order dependence upon halogen composition, a dependence which was accommodated by the previously established Pairwise Additivity Rule[1] (Chapter II).

Similar studies of octahedral halogen species of the Group VA and VB elements, niobium and antimony, were performed. In both systems, a second-order dependence of the chemical shift upon ligand composition was observed (in the absence of interfering chemical exchange). An extension of the pairwise additivity concept was developed (Chapter II) to accommodate these results. This latter application of pairwise additivity to the octahedral case provides a powerful empirical tool in that the identification of specific geometric isomers in solution is allowed.

An anomalous order of nuclear shielding was observed for titanium and niobium halogen species. This occurrence, however, did not effect the applicability of the pairwise rule.

The interpretation of the chemical shift data

obtained from the systems studied has proved to be most rewarding when performed on an empirical basis (see Summary, Chapter VII). Fewer successes were obtained upon attempts to interpret the observed data in terms of the quantum mechanical elements ascribed as defining the chemical shift phenomenon (Chapter IV and Vd).

The chemical shift phenomenon has its origin in the degree of magnetic shielding of a particular nucleus by its composite electrons when placed in a magnetic field. The electron density and distribution about a particular nucleus is dependent upon its molecular environment, and as such may be readily described in quantum mechanical terms. The works of Ramsey[2a-d], Schneider and Buckingham[3], Saika and Slichter[4] and Jameson and Gutowsky[5] agree on a basic format describing the chemical shift; that is a chemical shift expression composed of two parts, a diamagnetic and a paramagnetic (temperature-independent) term.

$$\delta = \sigma_d + \sigma_p$$

Until recently, the magnitude of the diamagnetic term (σ_d) for heavy nuclei has been assumed to be small and constant[5] as compared to the paramagnetic contribution to the chemical shift. Recent work by Mason (6 and references therein) indicates that that assumption is not entirely true.

The paramagnetic term, which has generally been assumed to control the observed shift ranges of heavy nuclei, consists of the following basic elements:

$$\sigma_p = -C\left(\frac{L(L+1)}{\Delta E}\left\langle\frac{1}{r^3}\right\rangle\right)$$

The two parameters favoured to control this term are the average energy, ΔE^{-1}, and the radial expansion of electrons, $\langle r^{-3}\rangle$. To date, most attempts to relate the theoretical model to observed shifts of the heavier elements have primarily considered $\langle r^{-3}\rangle$ and equated this variance with the nephelauxetic[7] series. Other interpretations have been based on ΔE^{-1}, in which the chemical shifts of a series of molecular species were assumed to vary as the inverse of the energy of their respective lowest lying electronic transitions.[40,41]

Such interpretations have stressed either ΔE^{-1} or $\langle r^{-3}\rangle$ as the controlling parameter and these approaches have met with success in select systems. However, a more general approach might involve consideration of both ΔE^{-1} and $\langle r^{-3}\rangle$ as competing parameters in σ_p, the latter of which in turn would compete with σ_d [6] to control the observed shift. Such an approach may eventually allow a complete explanation of the anomalous order of nuclear shielding experienced by titanium and niobium (Chapter IV and V

respectively). However, such complete theoretical interpretations must await more detailed knowledge of such factors as molecular orbitals and energy levels of species in question.

The principal aim of this research study therefore, has been the development and application of empirical aids to effect informative (and convenient) interpretation of the chemical shift parameter such that the latter may be more extensively employed as a chemical probe in systems of appropriate heavy nuclei.

CHAPTER II

THE PAIRWISE ADDITIVITY MODEL

In attempting to provide a theoretical interpretation for the composition dependence of any physical property of a molecule, the first-order approach to the problem generally is to try to evaluate substituent constants which can be summed to yield a calculated value for the desired property. Examples of this approach are the use of Pascal constants in the prediction of diamagnetic susceptibilities and the use of Hammett σ-parameters in predicting the dissociation constants of substituted benzoic acids. Only if this approach proves to be inadequate, as will be observed in the following chapters, is one forced to use a more sophisticated second-order approach which recognizes the influence of one substituent upon another.

A second-order approach which has met with success on a broad front in rationalizing and predicting the chemical shifts of a variety of nuclei is the Pairwise Additivity Model introduced by Vladimiroff and Malinowski[1]. By recognizing the change caused by one substituent in the wave function for all neighbouring substituents, this model

allows one to calculate the chemical shift for a central atom in a complex by the summing of pairwise interaction parameters for all substituents taken as adjacent pairs. This model has already been used successfully to rationalize the chemical shifts of boron-11[8], carbon-13[8] and aluminum-27[9] in four-coordinate tetrahedral environments. In these instances, the chemical shift of the central atom M in the tetrahedral compound is calculated by summing the six pairwise interaction parameters corresponding to the six edges of the tetrahedron. A first-order treatment of these tetrahedral compounds would involve summing only the four substituent constants for the ligands.

The present study constitutes the first application of the Pairwise Additivity Model to the chemical shift data from six-coordinate octahedral systems. The importance of establishing that the model can indeed be extended to the six-coordinate case lies in the fact that it provides an unambiguous method for identifying specific geometric isomers of six-coordinate complexes. Were the chemical shifts of the central atom M in such complexes a first-order function of ligand coordination only, such identifications would not have been possible.

The Pairwise Additivity Model applied to the generalized six-coordinate complex is best visualized in

terms of a ligand redistribution reaction occurring between MX_6 and MY_6 to give all seven redistribution products having stoichiometries MX_nY_{6-n} $(0 \leq n \leq 6)$. Because each of the MX_2Y_4, MX_3Y_3 and MX_4Y_2 complexes has two geometric isomers, however, the total number of different isomers possible is ten. The pairwise additivity parameters which must be evaluated for this system are η_{x-x}, η_{x-y}, η_{y-y} and once these are known, the chemical shift of M can be calculated by summing the appropriate combination of twelve interaction parameters corresponding to the twelve edges of the octahedral molecule in question. The manner in which this is done is illustrated in Table IV, pg. 39 for the specific case where X = Cl, Y = Br. The values of the three interaction parameters may be obtained from the observed chemical shift values for any three of the species MX_6, MX_5Y, MXY_5 and MY_6 through a consideration of the shift values and the appropriate coefficients of the interaction parameters. This may best be demonstrated in a solution to the following hypothetical data set:

Pairwise expression

Species	Defining Species	Chemical Shift (ppm)		
		Observed	Pairwise Calculated	Linear Approximation
(a) MX_6	$12\eta_{x-x} + 0\eta_{x-y} + 0\eta_{y-y}$	96	96	96
(b) MX_5Y	$8\eta_{x-x} + 4\eta_{x-y} + 0\eta_{y-y}$	108	108	112*
(c) MXY_5	$0\eta_{x-x} + 4\eta_{x-y} + 8\eta_{y-y}$	172	172	176*
(d) MY_6	$0\eta_{x-x} + 0\eta_{x-y} + 12\eta_{y-y}$	192	192	192

(a) $\eta_{x-x} = 8$ ppm. $= 96/12$

(d) $\eta_{y-y} = 16$ ppm. $= 192/12$

(b,c) $\eta_{x-y} = 11$ ppm. $= \frac{108-8\times8}{4}$ (b) $= \frac{172-8\times16}{4}$ (c)

The observed shifts do not agree with those obtained by a linear interpolation* (assuming seven species) between 96 and 192 ppm. Consequently, the observed shift data does not bear a strict first-order substituent-stoichiometry dependence. To evaluate a potential second-order dependence, a set of simultaneous equations is constructed with the observed shifts being made the dependent variables and equated to the summation of the three appropriate pairwise interaction parameters, each the product of a coefficient equal to the frequency of occurrence of the interaction in a particular species. These equations are then solved for the values of the pairwise interactions, the latter which have been treated as independent variables. The values obtained for the pairwise interactions are then employed to calculate the chemical shifts for comparison purposes, and as may be observed, complete agreement is attained.

Where one can observe more than the minimum number of resonance lines necessary to evaluate all the interaction parameters, the best η values are obtained by performing a multiple linear regression analysis by computer. This technique, being a least squares type of fitting, solves simultaneous equations of the following format,

$$y = C_0 + C_1X_1 + \ldots\ldots + C_nX_n$$

$$(\delta = C_0 + C_1\eta_1 + \ldots\ldots + C_n\eta_n)$$

where one such equation is entered for every species observed. Observed shifts, δ, are entered as the dependent variable, Y, and the coefficients of the appropriate pairwise interactions are entered as the coefficients of the independent variables, $X_1 \ldots X_n$, ($\eta_1 \rightarrow \eta_n$). Solutions are then produced for the pairwise interactions and C_0, the straight line intercept. The former are employed to calculate shift values, for comparative purposes, and the latter (C_0) is used in conjunction with the calculated standard errors of the interaction parameters to determine whether the computation errors are within the errors of the experiment.

The application of the Pairwise Additivity Model to a six-coordinate system involving three different ligands ([$NbCl_nBr_{5-n}$MeCN] pg.42) elicits another significant feature of the model. The η_{ij} values which are common to both the anion system $[NbCl_nBr_{6-n}]^-$ and the neutral molecular adduct system [$NbCl_nBr_{5-n}$·MeCN] (Chapter V pg. 44) involving three different ligands have been calculated independently in the two systems and are found to give the same parameter value in both systems. In using the Pairwise Additivity Model to assign spectral lines, it is important to know that the η_{ij} parameter values can be transferred without variation from one system to another of the same central atom and

coordination, independent of charge type.

It can be seen from Table IV, pg. 39, that cis and trans isomers of the same "molecule" give different combinations of the interaction parameter coefficients and hence are expected to give different chemical shifts for M. This phenomenon of isomer difference has already been observed in the ^{59}Co spectra for $[Co(NH_3)_4(N_3)_2]$ where the cis-isomer is shifted 230 ppm downfield from the trans-isomer[10]. In the present studies, the isomer difference phenomenon, used in conjunction with the Pairwise Additivity model which predicts the chemical shifts for all isomers whether observed or not, enables the identification of specific isomers where some are present and some are not.

The strict application of this model is based on the assumption that chemical exchange within the system of interest, whether inter- or intramolecular, is slow compared to the nmr time scale such that the chemical shift data employed in the analysis is not the result of exchange averaging, but of sterically-rigid discrete molecular species.

CHAPTER III

GERMANIUM-73 NMR SPECTRA OF GERMANIUM TETRAHALIDES

III.1 Introduction

Germanium is the sole Group IVB element to have previously escaped nmr study. Although carbon-13 has received the most study, silicon-29, tin-119 and lead-209 have all produced spectra suitable for establishing the chemical shift ranges experienced by these nuclei. Herein lies the first comprehensive nmr study of the ^{73}Ge nucleus, a study designed to establish the chemical shift range and the potential that this technique holds for eliciting structural information about germanium compounds.

The pattern and range of chemical shifts displayed by germanium-73 are consistent with those exhibited by other Group IV elements. The range in the case of the germanium tetrahalides spans 1117 ppm between $GeCl_4$ and GeI_4, which falls between the 1550 ppm range for the corresponding tin compounds and the 395 ppm range for the corresponding carbon compounds. In addition, the halogen-dependence pattern for the germanium shifts, with the tetraiodide

signal occurring to high field of the tetrachloride signal, is the same as that observed for the tetrahalo-compounds of the other main-group elements, such as ^{11}B[1], ^{13}C[12], ^{27}Al[13], ^{29}Si[14], ^{71}Ga[15], ^{115}In[16], and ^{119}Sn[17].

The germanium tetrahalides constitute the best series of model compounds for ^{73}Ge study as they compare directly with analogous compounds of the other Group IV elements which have received nmr study. At the same time it can be seen that the ^{73}Ge method provides the neatest means of characterizing the mixed tetrahalides of germanium. Previous Raman studies report the existence of all 15 of the tetrahalides involving chlorine, bromine, and iodine, and assign the different stoichiometries on the basis of the a_1 vibrational modes[18]. The relatively simple nmr spectra obtained for these systems confirm the earlier conclusions drawn from the more complex Raman spectra.

III.2 Results and Discussion

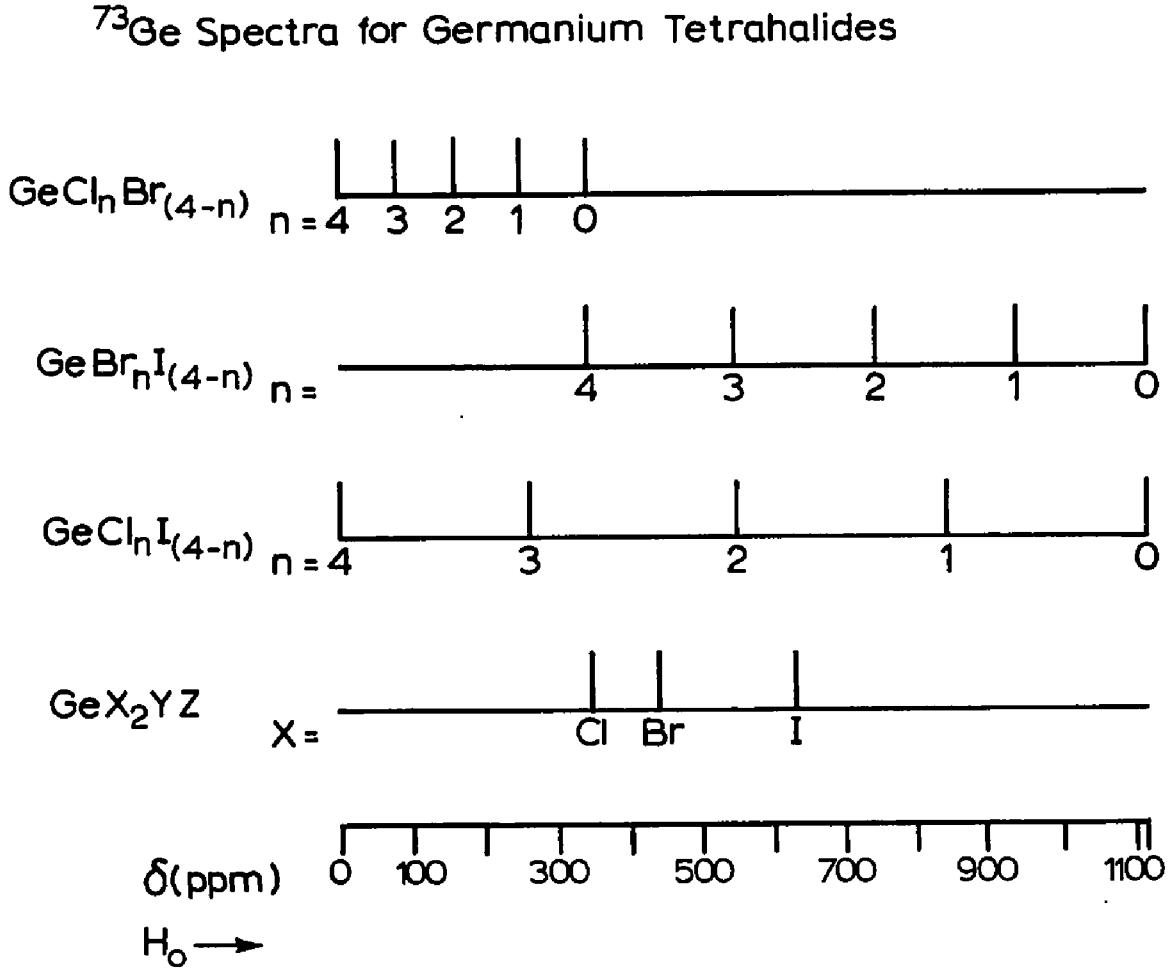
Single-line ^{73}Ge spectra have been obtained for $GeCl_4$ and $GeBr_4$ as neat liquids and for GeI_4 in carbon disulfide solution, from which chemical shifts for each of these three compounds have been obtained. The three separate 1:1 binary mixtures of the parent tetrahalides each give rise after equilibration to a 5-line ^{73}Ge

spectrum assignable to the 5 possible GeX_nY_{4-n} $(0 \leq n \leq 4)$ binary tetrahalogermanes arising from redistribution of halogen atoms. These three spectra are illustrated diagramatically in Figure 1. The relative signal intensities in each of these spectra appeared to be in the ratio 1:4:6:4:1 expected for random distribution of halogens. In order to observe the weakest signals, however, the irradiation power level had to be increased to a degree such that a valid comparison of signal intensities was not possible.

The 1:1:1 mixture of $GeCl_4$, $GeBr_4$, GeI_4/CS_2 gave rise, after a redistribution time of ten hours at room temperature, to a spectrum containing nine resonance lines. Six of these were assigned to $GeCl_3I$, $GeCl_2I_2$, $GeBr_2I_2$, $GeClI_3$, $GeBrI_3$, and GeI_4 on the basis of the spectral data obtained from the binary mixtures. The remaining three resonances at δ = 347, 438, 632 ppm. were assigned to $GeCl_2BrI$, $GeClBr_2I$, and $GeClBrI_2$ respectively. The intense resonance at 347 ppm. was assigned to $GeCl_2BrI$ since the equilibrium concentration of $GeBr_4$ (δ = 343 ppm.) in the mixture will be very small. The relationship of the line positions for these three ternary mixed halides to those for the binary mixed halides is illustrated in Figure 1.

FIGURE I

The ^{73}Ge nmr spectral line positions for the germanium tetrahalides.



The nuclear shielding of the germanium caused by the attached halogen atoms is consistent with the pattern of nuclear shielding already established for halogens bonded to other main group elements; namely, metal nucleus shielding increases in the order Cl < Br < I. If one assumes that each halogen makes a constant shielding contribution to the germanium nucleus, independent of that from the other three halogens present, as has been done for the tetrahalostannanes[17], the chemical shift for each of the mixed tetrahalogermanes can be calculated using the three single halogen shielding parameters δ'_X (X = Cl, Br, I) given in Table II and obtained from the expression $\delta'_X = {}^1/_4\ \delta_{GeX_4}$. The shifts calculated using this first-order theoretical approach are given in Table I under the heading "δ First Order" and are seen to involve deviations from the observed values as large as 18 ppm, with an average deviation for all twelve calculated shifts of 10 ppm. These deviations, which lie well outside the ±3 ppm uncertainty limits of the observed shifts, indicate the presence of a second-order effect upon the germanium shielding resulting from halogen-halogen interaction.

TABLE I

^{73}Ge CHEMICAL SHIFT VALUES[a]

Species	$\delta_{obs.}$[b] ppm.	Calculated Shifts: δ First Order	Dev'n.	Calculated Shifts: $\delta \Sigma c_{ij}\eta_{ij}$	Dev'n
$GeCl_4$	0	(0)	--	-1	1
$GeCl_3Br$	78	86	6	75	3
$GeCl_2Br_2$	161	172	11	158	3
$GeClBr_3$	250	257	7	248	2
$GeBr_4$	343	(343)	--	345	2
$GeCl_4$	0	(0)	--	0	--
$GeCl_3I$	262	279	17	268	6
$GeCl_2I_2$	549	559	10	545	4
$GeClI_3$	839	838	1	830	9
GeI_4	1117	(1117)	--	1123	6
$GeBr_4$	343	343	--	345	2
$GeBr_3I$	544	537	7	541	3
$GeBr_2I_2$	739	730	9	736	3
$GeBrI_3$	932	924	8	930	2
GeI_4	1117	(1117)	--	1123	6
$GeCl_2BrI$	347	365	18	352	5
$GeClBr_2I$	438	451	13	443	5
$GeClBrI_2$	632	644	12	637	5

[a] Relative to $GeCl_4$; positive values represent increased shielding and upfield shifts. [b] Error limits which include calibration uncertainty are ± 3 ppm.

TABLE II

Derived ^{73}Ge Shielding Parameters

First-Order Approximation			Pairwise Additivity Parameters		
δ'_{Cl}	=	0 ppm	η_{Cl-Cl}	$\simeq$	0 ppm
δ'_{Br}	=	85.8	η_{Br-Br}	=	57.8
δ'_{I}	=	279.3	η_{I-I}	=	187.3
			η_{Cl-Br}	=	25.4
			η_{Cl-I}	=	89.7
			η_{Br-I}	=	123.1
			intercept	=	-1.2

This second-order effect can be accommodated from the theoretical point of view by using the "pairwise additivity" model. Table II gives the six halogen pairwise additivity parameters which were obtained from the fifteen observed chemical shift values using a multiple linear regression analysis in which the six η parameters were treated as independent variables. Table I gives the fifteen chemical shift values calculated using this model. The values obtained compare sufficiently well with the observed values that the model can be used both to predict chemical

shift values for unobserved species within an observable system and to verify spectral assignments of observed lines within a many-line spectrum. In fact, the applicability of the model appears to be sufficiently good that it may well be that the calculated shift values (obtained by analysis of the complete set of experimental data) provide a better approximation to the true values than do individual values obtained experimentally.

Previous Raman studies[18] have identified the fifteen redistribution products of this germanium(IV) halide system. The redistribution products are reported to be inseparable[19], and the redistribution times for these species in solution are quoted to be "very fast"[18]. In the present study, where precautions to prevent hydrolysis were taken, very slow redistribution rates have been observed both with neat mixtures and with concentrated carbon disulfide solutions of germanium tetrahalides. Where the intensity changes of the ^{73}Ge resonance lines for a neat equimolar mixture of $GeCl_4$/ $GeBr_4$ were followed at 28°C, the time taken for the $GeCl_4$ signal to decrease to half its initial intensity was 250 minutes. In addition, the peak intensities in the five-line spectrum resulting at equilibrium are approximately those one calculates for a random Calingaert[20] distribution of halogens. A similar study of the tetrahalostannanes[17] shows

a random redistribution among the various possible tetrahalides but shows a rapid redistribution rate, although acknowledging that some hydrolysis might have occurred.

Titanium provided the next area of study, for titanium and germanium, being of the same period, possess similar oxidation states and halogen compounds. This furnished an excellent opportunity to compare superficially analogous main- and transition-group compounds, in particular those of d^0 and d^{10} T_d configuration.

CHAPTER IV

TITANIUM-47 AND TITANIUM-49 NMR SPECTRA OF TITANIUM(IV)-HALOGEN COMPOUNDS

IV.1 Introduction

Sufficient incentive to study the nmr spectra of titanium tetrahalides was readily available. The initial incentive was, of course, the anticipated analogy with the germanium system. In addition however, there has been some recent discussion in the literature concerning the state of aggregation of liquid titanium(IV) tetrachloride. Griffiths[34] has interpreted the results of Raman studies to imply that $TiCl_4$ is dimeric in the liquid state and monomeric in solution in carbon tetrachloride. A subsequent detailed study[35] of the intensity pattern of the a_1 vibrational mode of $TiCl_4$ has provided evidence that $TiCl_4$ is monomeric both as a pure liquid and in cyclohexane solution. We have investigated this problem using $^{47,49}Ti$ nmr and obtained results consistent with the existence of monomeric units in liquid $TiCl_4$. Similar observations were made for the analogous titanium(IV) tetrabromide system.

The utility of the nmr method in determining the

nature of the products of redistribution reactions has been amply demonstrated for a variety of systems (e.g., $SnCl_4$-$SnBr_4$-SnI_4,[17] $POCl_3$-$POBr_3$,[28] and $AlCl_4^-$-$AlBr_4^-$-AlI_4^- [13]). Mixtures of $TiCl_4$ and $TiBr_4$ are known to contain an essentially random distribution of all possible species, $TiCl_4$, $TiCl_3Br$, $TiCl_2Br_2$, $TiClBr_3$ and $TiBr_4$.[35] We were unable to obtain $^{47,49}Ti$ chemical shift data for the individual mixed species, as in the germanium study, due to rapid exchange between the species.

Extensive chemical shift data for the nmr of various atoms in tetrahedral or pseudo-tetrahedral halogen-containing environments has been reported in recent years. Apparently without exception, the order of increasing shielding of the nucleus under investigation is Cl < Br < I. In particular, the nuclei for which this trend has been found are ^{11}B,[11,21] ^{13}C,[11,22-26] ^{27}Al,[13] ^{29}Si,[14,27] ^{31}P,[28,29] ^{71}Ga,[15] ^{115}In,[16] and ^{119}Sn[17]. While investigating the feasibility of using $^{47,49}Ti$ nmr to derive information on structure and bonding in titanium compounds, we have obtained surprising chemical shift data for the titanium(IV) tetrahalides. Our results show that the order of increasing nuclear magnetic shielding is anomalous, viz, I, Br < Cl.

Previous workers have observed $^{47,49}Ti$ nmr signals in liquid $TiCl_4$[31,32], aqueous H_2TiF_6[31] and in the solids

$SrTiO_3$, TiCo, TiFe and TiH_2 [33].

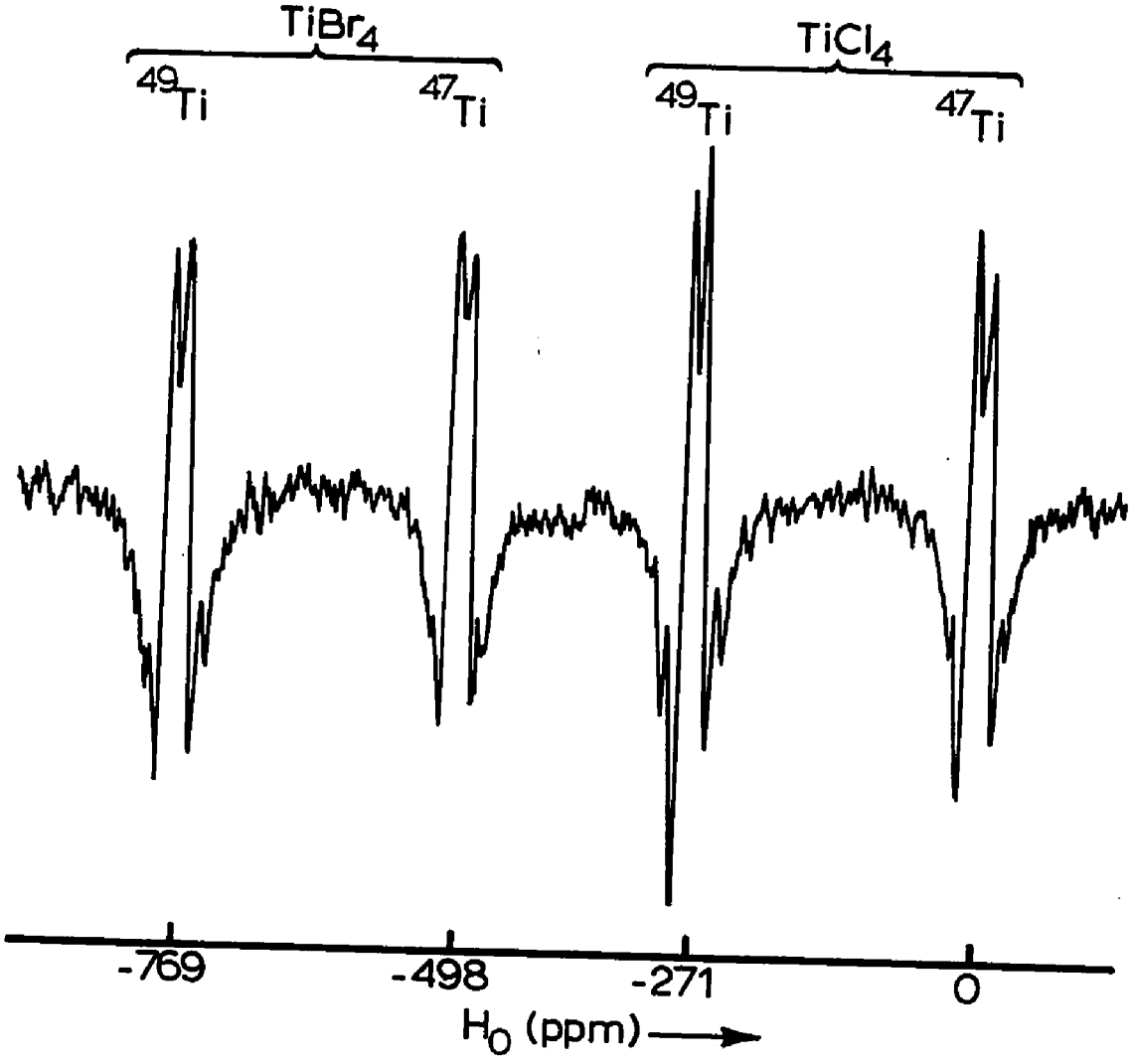
IV.2 Results

The $^{47,49}Ti$ nmr spectra of $TiCl_4$ and $TiBr_4$ are shown in Fig. II. The separation between the ^{47}Ti and ^{49}Ti resonances in each compound was found to be 271 (±3) ppm, in good agreement with earlier studies.[31,32] Signals for $TiBr_4$ were found at 498 (±5) ppm downfield from $TiCl_4$. Solutions of $TiCl_4$ and $TiBr_4$ in both cyclohexane and carbon tetrachloride (20 mole %) gave signals which were unshifted from those of the neat liquids. We were unable to detect a signal for TiI_4 either as a solid or in solution (see experimental section).

Two mixtures of neat titanium(IV) tetrahalides were studied: $TiCl_4$-$TiBr_4$ and $TiCl_4$-TiI_4. Although $TiBr_4$ is a solid at room temperature, addition of even small amounts of the tetrachloride produced a homogeneous liquid. The $^{47,49}Ti$ nmr spectra of these mixtures showed just one resonance (for each isotope), the chemical shift of which varied linearly with the mole fraction of the tetrabromide (Table III, Figure III). The line width was noticeably broader than those for $TiCl_4$ and $TiBr_4$ run under the same instrumental conditions. Titanium(IV) tetraiodide was only sparingly soluble in liquid $TiCl_4$. A mixture nominally 0.8 mole fraction in $TiCl_4$ consisted of a red-brown liquid and

FIGURE II

The ^{47}Ti and ^{49}Ti nmr spectra of $TiCl_4$ and $TiBr_4$*



* Spectra recorded as the derivative of the dispersion mode. The splitting of each resonance is due to over-modulation at 40 Hz.

TABLE III

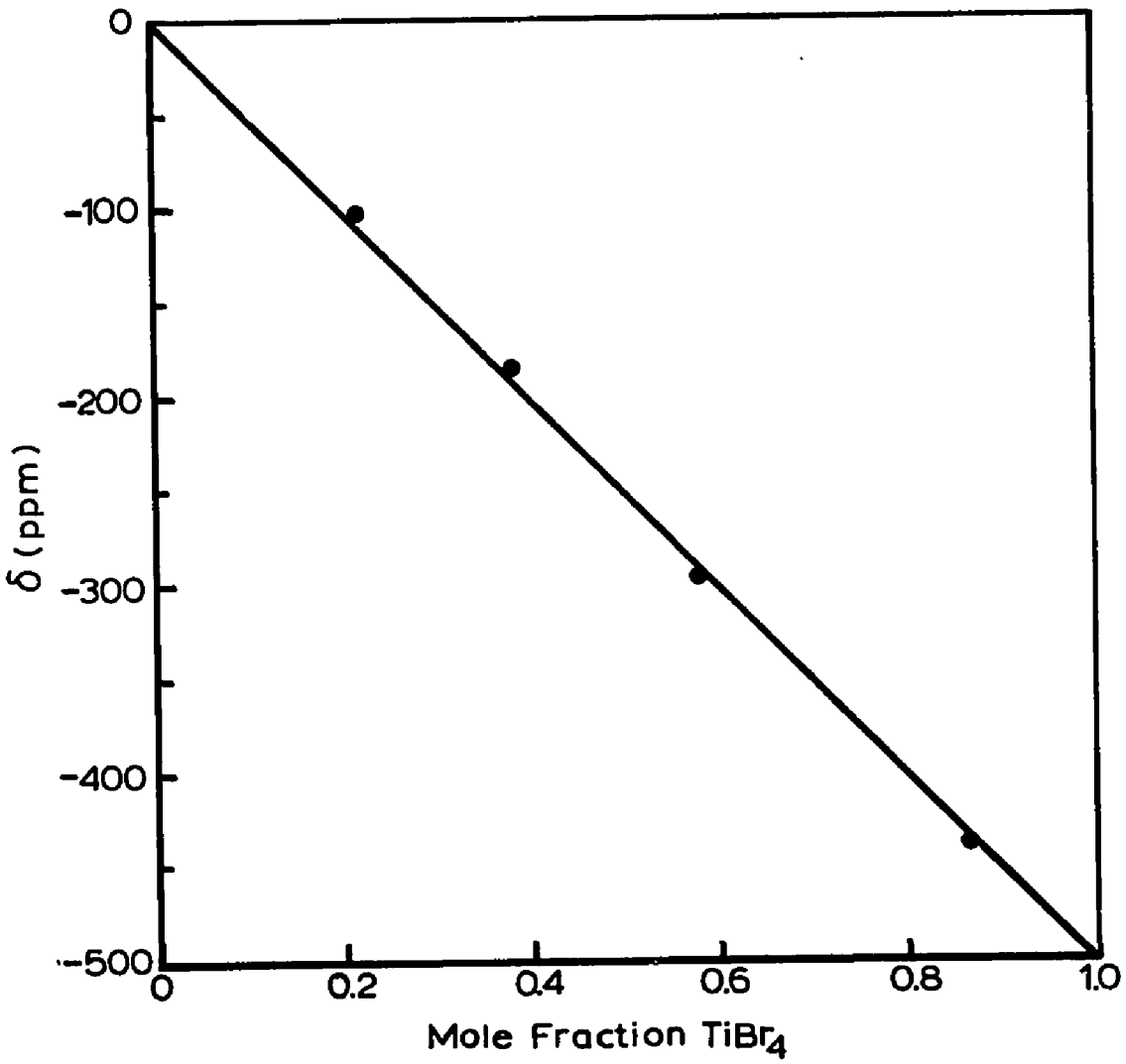
$^{47,49}Ti$ Chemical Shifts of $TiCl_4/TiBr_4$ Mixtures

δ (ppm)	χ_{TiBr_4}
0	0
-103	0.220
-185	0.383
-295	0.580
-438	0.864
-498	1.0

$$\delta = -505.9\ \chi_{TiBr_4} + 3.8 \quad \text{(Least Squares Fit)}$$

FIGURE III

Plot of chemical shift vs mole fraction of $TiBr_4$ for $TiCl_4$-$TiBr_4$ mixture.



undissolved TiI_4. A resonance signal was observed for this mixture at 58 (±7) ppm downfield from $TiCl_4$. Failure to observe any shift in the signal for $TiBr_4$ on adding TiI_4 to a solution of the bromide in carbon tetrachloride was probably due to the low solubility of TiI_4 in this solvent.

A solution of titanium(IV) fluoride in 48% aqueous HF gave a signal 1177(±7) ppm upfield from $TiCl_4$. The shift was independent of TiF_4 concentration in the range 0.8M, the lower limit of detection, to 3.4M. The resonance linewidths were larger than those for $TiCl_4$ and $TiBr_4$. Similar unshifted signals were observed for aqueous solutions of TiF_4 and ammonium fluoride in 1:1 and 1:2 mole ratios, but no resonance was detected for an aqueous solution of TiF_4.

IV.3 Discussion

The observation that the $^{47,49}Ti$ nmr signals of $TiCl_4$ and $TiBr_4$ are unshifted by dilution in inert solvents supports the existence of monomeric units in the neat liquids. The assignment of the vibrational spectra of $TiCl_4$ and $TiBr_4$ in inert solvents in terms of the selection rules for tetrahedral symmetry appears to be generally accepted.[34,35] Molecular association in the pure liquids would necessitate a lowering of the symmetry from T_d and an increase in the coordination number of titanium to five or six. It is anticipated that such changes would be reflected in the

^{47,49}Ti nmr spectra. The range of chemical shifts of titanium(IV) compounds measured in this study is about 2000 ppm. Shift ranges of comparable magnitude have been observed in the nmr spectra of many of the other heavier nuclei[36] and in these systems, changes in coordination number and symmetry are found to produce large changes in resonance position. It is therefore unlikely that the titanium nucleus in two different structural environments would give rise to a resonance absorption in precisely the same position. Thus we conclude that the same species (i.e. monomeric, tetrahedral $TiCl_4$ or $TiBr_4$) is responsible for the signals in the neat liquids and in solution. Qualitative observations of line widths and intensities for the spectra are consistent with this conclusion.

The results for the mixtures of $TiCl_4$ and $TiBr_4$ indicate rapid chemical exchange of halogen atoms between the five species present[35] such that the titanium nuclei experience an average environment. Assuming that the chemical shifts of the mixed species increase in a roughly linear manner with progressive substitution of bromine for chlorine, the average lifetimes of the species can be estimated[37] as less than 5×10^{-3} sec.

A similar exchange process probably takes place between two or more species in the $TiCl_4$-TiI_4 mixture since only one signal was observed. The position of this resonance strongly suggests that the shift for TiI_4, if observable, would be downfield from $TiCl_4$.

The anomalous order of relative shielding at the titanium nucleus observed for titanium(IV) tetrahalides provides an interesting example of a departure from the usual relative magnitudes of the parameters which contribute to nuclear screening variation consequent on changing the ligands. The nuclear magnetic shielding can be expressed as the sum of diamagnetic and paramagnetic, $\underline{\sigma}_p$, contributions[2(b)]. For atoms other than hydrogen, the diamagnetic term is generally assumed to vary little from compound to compound[5], although recent work[6,38] indicates that this assumption may not be entirely correct. Normally considered the dominant contribution to the shielding, $\underline{\sigma}_p$ can be expressed in the form[5]

$$\underline{\sigma}_p = -(2\underline{e}^2\underline{\hbar}^2/3\Delta\underline{m}^2\underline{c}^2)(\langle 1/\underline{r}^3\rangle_{p}\underline{P}_u + \langle 1/\underline{r}^3\rangle_{d}\underline{D}_u)$$

where Δ is the average excitation energy for the molecule, $\underline{P}_u$ and $\underline{D}_u$ are the respective 'unbalance' of the valence electrons in the p and d orbitals and $\langle 1/\underline{r}^3\rangle_p$, $\langle 1/\underline{r}^3\rangle_d$ are the average values of the inverse cube radii of the p and d orbitals respectively.

Both $\underline{P}_u$ and $\underline{D}_u$ depend on the hybridization of the bonding orbitals and on the ionicity of the bonds.[5] It is not apparent how these parameters will vary for the titanium(IV) tetrahalides although it is reasonable to assume that the term $\langle 1/\underline{r}^3 \rangle_p \underline{P}_u$ is relatively unimportant because the hybridization is d^3s with a slight admixture of sp^3 [39].

Of the remaining terms, $\langle 1/\underline{r}^3 \rangle_d$ increases from TiI_4 to $TiBr_4$ to $TiCl_4$ consistent with the trend in electron delocalization expected from the nephelauxetic series.[7] Domination of σ_p by this term would imply an increase in shielding in the order Cl < Br < I. This is the order observed for tetrahedral halides of the main group elements. The variation of the magnitude of σ_p for the titanium(IV) tetrahalides, however, is qualitatively consistent with the decreasing values of Δ as approximated by the energies of the long wavelength electron transfer transitions, viz, $TiCl_4$; 34,840 cm^{-1}; $TiBr_4$, 28,680 cm^{-1}; TiI_4, 19,400 cm^{-1} [35]. While tetrahedral compounds of main group elements exhibit a similar bathochromic shift as the ligands vary from Cl^- to Br^- to I^-, it is significant that the energies of the long-wavelength electron transfer transitions are generally about 10,000 cm^{-1} or more higher than for the corresponding titanium compounds. Thus, the titanium(IV) tetrahalides present a situation similar to that of symmetrical, octa-

hedral complexes of cobalt(III) where a good correlation has been found between ^{59}Co chemical shifts and the energy of the relatively low-lying $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions.[40,41]

The resonance observed for the solutions containing titanium(IV) tetrafluoride is due to the hexafluorotitanate(IV) ion. This was confirmed by obtaining ^{19}F nmr spectra of the same solutions. TiF_4 in 48% aqueous HF showed just two ^{19}F absorptions at -152.3 ppm and +92.2 ppm (relative to trifluoroacetic acid). The position of the low field absorption agrees well with that obtained previously for TiF_6^{2-} (+ 152.2 ppm)[42] while the high field signal is attributed to F^- in 48% aqueous HF. The aqueous solutions of TiF_4 and NH_4F gave one signal at -152.6 ppm. We found no evidence for the instability of TiF_6^{2-} noted in previous work[31]. The broadening of the $^{47,49}Ti$ signals, relative to $TiCl_4$, is probably due to unresolved spin-spin coupling between titanium and fluorine nuclei. The ^{49}Ti-^{19}F coupling constant has been determined[42] from the ^{19}F nmr of $(NH_4)_2TiF_6$ in aqueous solution as 33 Hz and the ^{47}Ti - ^{19}F coupling constant will have a value close to this. Thus, each of the ^{47}Ti and ^{49}Ti resonances should consist of seven lines covering a total of about 200 Hz. The observed line widths were about 220 Hz.

Of particular interest in this study was the anomalous shielding of the tetrahedral Ti(IV) d^0 nucleus, as compared with Ge(IV) d^{10}. One of the available extensions of these studies of Group IV fourth period nuclei was to investigate the Group V fifth period elements, Nb(V) d^0 and Sb(V) d^{10}. One of the attractive properties of the latter two elements was their propensity to attain octahedral coordination.

CHAPTER V

NIOBIUM-93 NMR SPECTRA OF HEXA-COORDINATE NIOBIUM(V) SPECIES

V.A Niobium-93 NMR Study of Hexachlorobromoniobates and Pentachlorobromoniobium-Acetonitrile Adducts.

V.A.1 Introduction

The state of $NbCl_5$ and $NbBr_5$ in acetonitrile solution has long been a topic of controversy. It is generally accepted that they exist as pseudo-octahedral halogen-bridged dimers in the solid state[43,44]. Kepert and Nyholm found that $NbCl_5$ exists as a 1:1 acetonitrile adduct in acetonitrile[45]. Later workers, however, interpreted the charge transfer spectra of $NbCl_5$ in acetonitrile as that of the chlorine-bridged dimer[46]. Recently, an intensive vibrational study of $NbX_5 \cdot NC \cdot CY_3$ (X = Cl or Br; Y = H or D) in the solid state and in acetonitrile solution by Ozin and Walton[47] leaves little doubt that these species are six coordinate, molecular, and monomeric.

The $NbCl_6^-$ and $NbBr_6^-$ ions have also been prepared and are well characterized[46,48-50], generally as the tetraalkylammonium salts prepared from the appropriate thionyl

halide. In addition, the ions $[NbX_5Y]^-$ (X = Cl or Br; Y = Cl, Br, or I) have been prepared and characterized as the tetraethylammonium salts[51]. Compounds of the type $Et_4N[NbX_4Y_2]$ could not, however, be isolated[51].

Much of the controversy associated with the nature of niobium(V) halides in solution has arisen because of the difficulty in characterizing the species present, coupled with their propensity for hydrolysis. We now wish to report an improved method for characterizing niobium(V) halides in solution based upon their ^{93}Nb nmr spectra. Comprehensive studies of both the $[NbCl_nBr_{6-n}]^-$ system ($0 \leq n \leq 6$) and the $[NbCl_nBr_{5-n}\cdot MeCN]$ system ($0 \leq n \leq 5$) are here reported in which all possible stoichiometries in each system have been prepared and the natures of the geometric isomers present are characterized. A controlled hydrolysis experiment has been carried out which clarifies the relationship between the $[NbCl_nBr_{6-n}]^-$/MeCN system and the $[NbCl_nBr_{5-n}\cdot MeCN]$ system. By using the ^{93}Nb spectral data obtained in this study, we have extended the Pairwise Additivity Model developed by Vladimiroff and Malinowski[1] from the 4-coordinate to the 6-coordinate case where its applicability is sufficiently good to enable one to distinguish unambiguously <u>cis</u> from <u>trans</u> geometric isomers.

V.A.2 The $[NbCl_nBr_{6-n}]^-$ System

The ^{93}Nb spectrum of an equimolar mixture of $Et_4N[NbCl_6]$ and $Et_4N[NbBr_6]$ allowed to equilibrate in acetonitrile solution for 1 hour consists of 7 lines as shown in the top spectrum of Figure IV. Each line has been assigned to one of the seven possible stoichiometric molecules $[NbCl_nBr_{6-n}]^-$ where $0 \leq n \leq 6$; The specific assignments given in Table IV have been made by interpolating in a sequential manner the lines for the mixed hexahalides between the observed values for the single line spectra obtained from $[NbCl_6]^-$/MeCN and $[NbBr_6]^-$/MeCN solutions. These assignments are consistent with those given recently by Buslaev et al.[52] and our chemical shift values obtained at 14.67 MHz agree with those obtained earlier at 6 MHz within experimental uncertainty*.

---

* Buslaev et al.[52] obtained their $[NbCl_nBr_{6-n}]^-$ data from a solution prepared by dissolving $NbCl_5$ and $NbBr_5$ in acetonitrile. In the absence of added halide ion, this solution could only have yielded hexahaloniobate(V) ions through adventitious hydrolysis since the disproportionation reaction $2MX_5 \cdot MeCN \rightarrow MX_4 \cdot 2MeCN^+ + MX_6^-$ does not occur[47]. On the other hand, if acetonitrile (1 mole MeCN per mole of Nb) is added to a suspension of Nb_2Cl_{10} in CH_2Cl_2 a clear yellow solution develops immediately from the two phase mixture. ^{93}Nb NMR indicates the only Nb species present to be $[NbCl_5 \cdot MeCN]$.

FIGURE IV

The ^{93}Nb nmr spectra of $[NbCl_nBr_{6-n}]^-$

and $[NbCl_nBr_{5-n}\cdot MeCN]$ Systems

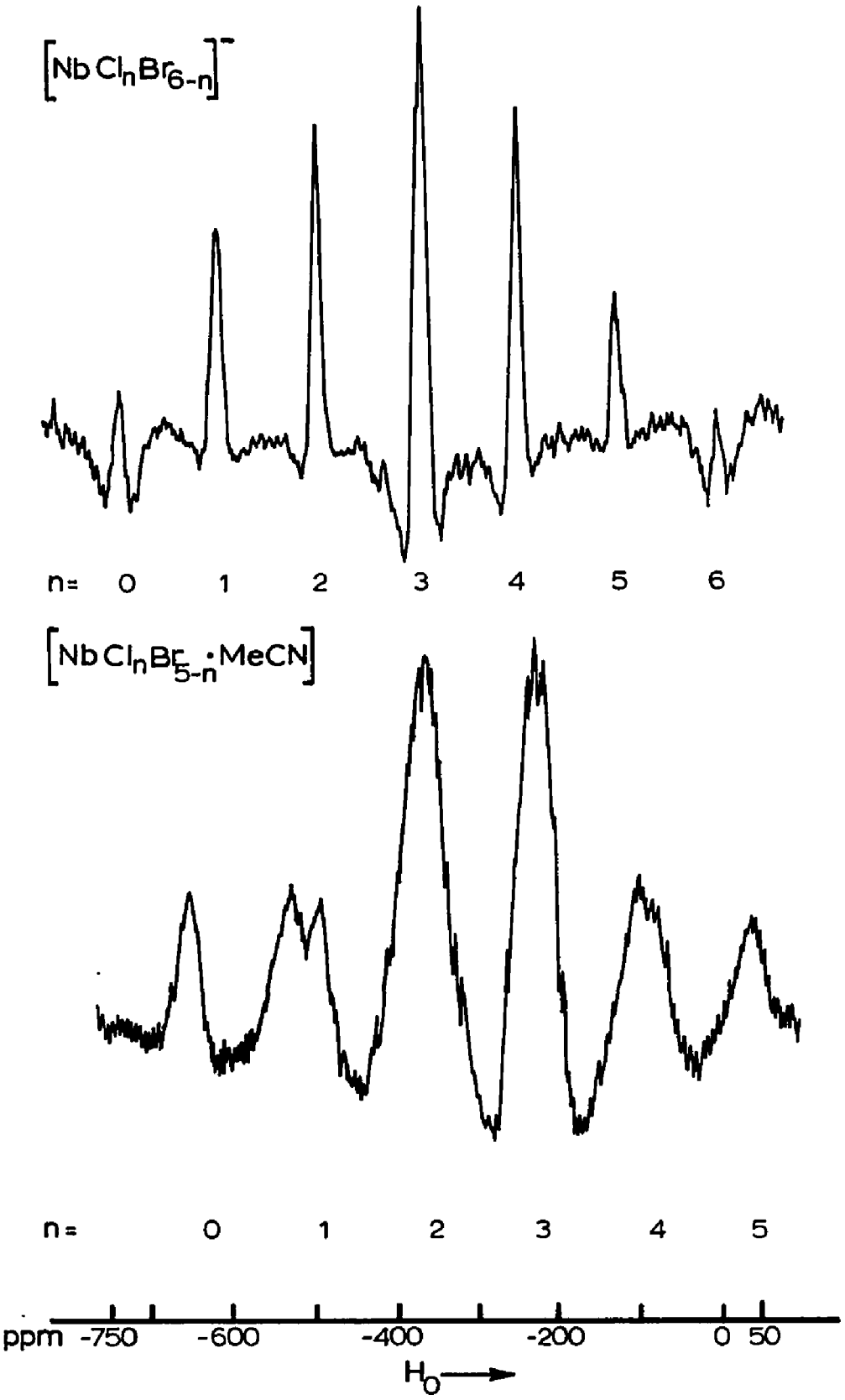

[NbCl$_n$Br$_{6-n}$]$^-$
n= 0 1 2 3 4 5 6
[NbCl$_n$Br$_{5-n}$·MeCN]
n= 0 1 2 3 4 5
ppm -750 -600 -400 -200 0 50
H_0

TABLE IV

^{93}Nb Shifts for $[NbCl_nBr_{6-n}]^-$ Species in MeCN

Species		Additivity Coefficients Cl-Cl	Cl-Br	Br-Br	$\delta_{calc.}$ $\Sigma c_{ij}\eta_{ij}$	$\delta_{obs.}$[a] ppm	$\delta_{calc.}$ First Order
$NbCl_6^-$		12	0	0	- 0.4	0	0
$NbCl_5Br^-$		8	4	0	-132	-132	-122
$NbCl_4Br_2^-$	cis	5	6	1	-258	-258	-244
	trans	4	8	0	-263		
$NbCl_3Br_3^-$	cis	3	6	3	-380	-380	-366
	trans	2	8	2	-385		
$NbCl_2Br_4^-$	cis	1	6	5	-502	-501	-487
	trans	0	8	4	-507		
$NbClBr_5^-$		0	4	8	-619	-621	-609
$NbBr_6^-$		0	0	12	-732	-731	-731

Additivity Parameter Values

$$\eta_{Cl-Cl} \simeq 0 \text{ ppm}$$

$$\eta_{Cl-Br} = -32.8$$

$$\eta_{Br-Br} = -60.9$$

[a]Error limits on observed chemical shifts are ±2 ppm. It is illuminating to note that successive substitution of Br for Cl causes a downfield shift. This anomalous shift direction has also been observed in the halogen dependence of ^{47,49}Ti Shifts[53].

Because there are two geometric isomers for each of $[NbCl_2Br_4]^-$, $[NbCl_3Br_3^-]$, and $[NbCl_4Br_2]^-$, a total of ten lines in the nmr spectrum might be anticipated corresponding to the ten different molecules which can in principle be accommodated within the seven possible $[NbCl_nBr_{6-n}]^-$ stoichiometric species. The fact that only seven ^{93}Nb resonances are observed could be due to one or more of the following factors:

(i) accidental degeneracy resulting in two different isomers having the same chemical shift.

(ii) a kinetic isomerization process occurring rapidly on the nmr time scale giving rise to a single averaged signal for both cis and trans isomers

(iii) certain isomers being thermodynamically more stable than others such that not all six isomers from the three geometric pairs exist in detectable concentrations in solution.

The following discussion shows that (iii) is the operative factor in the present case.

Factor (i) can be ruled out from our knowledge of the dependence of ^{93}Nb shift on its coordinative environment. That the ^{93}Nb shift is not a linear function of the coordination composition can be seen from Table 1, where the agreement between observed shifts and those calculated using a

first-order model is seen to be poor. The agreement between observed and calculated values using the Pairwise Additivity model indicates the ^{93}Nb shift depends not only upon coordination composition but also upon coordination geometry. Data in Table I indicate a minimum difference of 5 ppm between cis and trans isomers of the same coordination composition, which difference is capable of resolution with the present instrumentation. Factor (ii) can be ruled out on the basis of our knowledge of halogen exchange rates at niobium(V) along with the observed line shapes and positions within this spectrum. By observing the growth of the ^{93}Nb lines in the spectrometer as the redistribution reaction proceeds, it can be seen that the rate of intermolecular halogen exchange is slow on the nmr time scale. This does not, however, rule out the possibility of an intramolecular rearrangement leading to isomerization which might be more rapid. To rule out this possibility, the lineshapes observed for the n = 2,3,4 cases show no evidence of distortion which could be attributed to exchange broadening. Thus if isomerization is occurring, it is doing so at a rate sufficiently rapid to give "sharp" lines whose positions are definitive. The comparison in Table IV of the calculated line positions with the observed positions based on the assumed presence of only one geometric isomer shows agreement within 1 ppm.

If a rapid isomerization process were occurring, the observed line position would represent the weighted average for the static isomers, these two line positions would be in poor agreement with the calculated values. The weight of evidence therefore indicates that factor (ii) is not operating.

Having accepted the fact that for each of $[NbCl_2Br_4]^-$, $[NbCl_3Br_3]^-$, and $[NbCl_4Br_2]^-$, one geometric isomer predominates to the virtual exclusion of the other, we are then faced with the problem of identifying, in each case, which isomer this is. To accomplish this we require a theoretical model capable of reflecting the geometric dependence of the metal-atom chemical shift in a six-coordinate complex. The Pairwise Additivity Model which has been successfully applied to metal-atom shifts in four coordinate complexes possesses this added capability when extended to the six-coordinate case. Theoretical chemical shift values calculated as shown in Table IV for the six isomers from the three cis-trans pairs indicate that in every case only the cis-isomer is present in solution.

V.A.3 The $[NbCl_nBr_{5-n}\cdot MeCN]$ System

By dissolving either Nb_2Cl_{10} or Nb_2Br_{10} in acetonitrile solution under anhydrous conditions, a solution results which gives rise to a single broad ^{93}Nb resonance

line which can only be assigned to the solvent adduct $[NbX_5 \cdot MeCN]$.

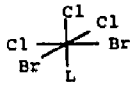
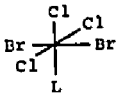
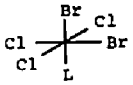
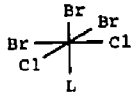
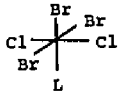
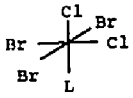
Adduct	^{93}Nb shift, ppm	Linewidth, Hz.
$NbCl_5 \cdot MeCN$	+ 49	ca. 500
$NbBr_5 \cdot MeCN$	-640	ca. 500

By mixing equivalent amounts of the anhydrous $[NbCl_5 \cdot MeCN]$ and $[NbBr_5 \cdot MeCN]$ solutions, a new solution giving a seven-line ^{93}Nb spectrum results, as shown at the bottom of Figure IV. The assignments of these spectral lines to the six possible stoichiometries in the system $[NbCl_nBr_{5-n} \cdot MeCN]$ $(0 \leq n \leq 5)$ are given in Table V. An identical spectrum was observed for a solution of $Nb_2Cl_{10}/Nb_2Br_{10}/4MeCN$ in CH_2Cl_2, the only difference being that all resonances were shifted downfield by 27±3 ppm. Such solvent shifts are not unusual, and generally signify greater stabilization of either the ground or excited electronic states of a species in one solvent relative to the other. The intensities of all observed lines are approximately those anticipated for the 1:5:10:10:5:1 random distribution of two ligands among five coordination positions.

All of these solutions produced identical spectra after standing for two weeks. This indicates the absence of hydrolysis or any auto-ionization process capable of producing $[NbX_nY_{6-n}]^-$ species in sufficient concentration

TABLE V

^{93}Nb Shifts for [$NbCl_nBr_{5-n}$·MeCN] Species in MeCN

Species	Additivity Coefficients Cl-Cl	Cl-Br	Br-Br	Cl-MeCN	Br-MeCN	$\delta_{calc.}$ $\sum c_{ij}\eta_{ij}$	$\delta_{obs.}$[a] ppm	$\delta_{calc.}$ First Order
$NbCl_5$·MeCN	8	0	0	4	0	+ 48	+ 49	+ 49
$NbCl_4Br$·MeCN								
cis	5	3	0	3	1	-100		- 89
trans	4	4	0	4	0	- 84	- 90	
$NbCl_3Br_2$·MeCN								
	3	4	1	2	2	-243		
	2	6	0	2	2	-248		-227
	2	5	1	3	1	-225	-229	
$NbCl_2Br_3$·MeCN								
	1	4	3	2	2	-364	-354	
	0	6	2	2	2	-369		-364
	1	5	2	1	3	-386		
$NbClBr_4$·MeCN								
cis	0	3	5	1	3	-503	-496	
trans	0	4	4	0	4	-524	-529	-502
$NbBr_5$·MeCN	0	0	8	0	4	-636	-640	-640
$NbCl_6^-$	12	0	0	0	0	- 0.7	0	
$NbBr_6^-$	0	0	12	0	0	-730	-731	

Additivity Parameter Values

$\eta_{Cl-Cl} \simeq 0$ ppm

$\eta_{Cl-Br} = -32.8$

$\eta_{Br-Br} = -60.8$

$\eta_{Cl-MeCN} = 12.0$

$\eta_{Br-MeCN} = -37.3$

[a] Error limits on observed chemical shifts are ± 5 ppm.

to be detected.

Addition of small amounts of "wet" acetonitrile or free halide ion to the $[NbCl_nBr_{5-n}\cdot MeCN]$ solution in acetonitrile results in the appearance of another series of sharper resonance lines ($\nu_{\frac{1}{2}} \leq 100$ Hz) characteristic of the $[NbCl_nBr_{6-n}]^-$ system coexisting with the relatively broad resonances ($\nu_{\frac{1}{2}} \approx 500$ Hz) due to the MeCN adduct species. If sufficient halide ion or "wet" acetonitrile are added, only the seven-line $[NbCl_nBr_{6-n}]^-$ spectrum is observed. Similar treatment of the $[NbCl_nBr_{5-n}MeCN]$ system in dichloromethane solution with "wet" dichloromethane results in a gradual collapse of the ^{93}Nb spectrum and simultaneous formation of a precipitate in the same tube. [Nb_2X_{10} and NbX_6^-; X=Cl,Br, are sparingly soluble in CH_2Cl_2.]

It is evident that the agreement between the observed shift values and those calculated using the Pairwise Additivity Model is not as good as in the previous system where there are only two different types of substituent on the niobium atom. The increased error limits on the latter set of data result in large part from the broader resonance

lines* observed for the $[NbX_nY_{5-n}\cdot MeCN]$ system (ca. 500 Hz vs. ca. 100 Hz for the $[NbX_nY_{6-n}]^-$ anions) making the determination of line position less precise. Even with the increased error limits, however, it is still possible to assign the signals for cis and trans isomers of $[NbClBr_4\cdot MeCN]$.

By using the Pairwise Additivity Model, structural information about the MeCN adducts in acetonitrile solution is readily extracted. A transfer of the η_{ij} parameter values from the $[NbCl_nBr_{6-n}]^-$ system permits a calculation of $\eta_{Cl\text{-}MeCN}$ and $\eta_{Br\text{-}MeCN}$ values from the observed shifts of the pentachloride and pentabromide adducts respectively. Using these parameter values, a preliminary set of chemical shifts for the twelve possible structures of the six stoichiometries were calculated. A basis matrix containing the structure coefficients and the observed chemical shifts was then subjected to a multiple linear regression analysis to obtain the best values for the η_{ij} parameters. The results are presented in Table V. These show that in the case of $NbClBr_4\cdot MeCN$, both the cis and trans isomers are present.

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* Because of its large electric quadrupole moment, the niobium nucleus experiences increased quadrupolar relaxation and hence increased linewidth in the presence of an increased electric field gradient. The substitution of an MeCN molecule for a halogen in a hexahaloniobate ion will provide this electrical asymmetry.

In the other cases where more than one geometric isomer is possible, only one isomer is observed.

V.A.4 Geometric Preferences

The $[NbCl_nBr_{6-n}]^-$ System. If viewed on a purely steric basis, the preference for cis configurations displayed by this system might appear surprising. The results are, however, consistent with a pattern already established for six-coordinate tin halides $[SnX_nY_{6-n}]^{2-}$ and titanium halides $[TiX_nY_{6-n}]^{2-}$. Infrared and Raman studies indicate the adoption of cis configurations by $SnCl_4Br_2]^{2-}$, $[SnCl_4I_2]^{2-}$, $[SnCl_2Br_4]^{2-}$, and $[SnCl_2I_4]^{2-}$ in the solid state[54].

Similar evidence has been adduced to indicate cis configurations for $[TiCl_2Br_4]^{2-}$ and $[TiCl_4Br_2]^{2-}$ [54]. Studies by ^{19}F nmr show that $[SnF_4X_2]^{2-}$ species (X=Cl,Br,I) favour the cis over the trans configuration, the preference increasing from Cl to Br to I [55].

The presently accepted view is that this preference for cis configurations results from the enhanced π-bonding which can occur relative to that which might be possible in the trans isomer[54,56,57]. This argument runs that in the trans isomer, the better π-donor ligands compete for the same empty t_{2g} orbital on the metal. This is not, however, the only possible explanation. It could be that the

distance between adjacent bromines is such that they lie on the attractive rather than the repulsive portion of the van der Waals energy curve.

The $[NbCl_nBr_{6-n}\cdot MeCN]$ System. In the $[NbCl_nBr_{6-n}]^-$ system, it was noted that cis-geometries are preferred to trans. Alternatively, one can say that Br prefers to be trans to Cl rather than to Br. The order of stability is then (Br trans to Cl) > (Br trans to Br). A similar analysis of the observed isomeric preferences in the MeCN adduct system indicates the following order of stability*: (Br trans to MeCN) > (Br trans to Cl) > (Cl trans to MeCN) ≈ (Br trans to Br).

* There is one outstanding exception to this trend; that is the resonance at -529 ppm which is assigned to trans[$NbCl-Br_4\cdot MeCN$].

V.B Hexathiocyanato-isothiocyanato-chloroniobates, $[Nb(SCN)_n(NCS)_mCl_{(6-(n+m))}]^-$.

V.B.1 Introduction

The ambidentate nature of the thiocyanate ion is clearly demonstrated by the present niobium-93 nmr studies of $[NbCl_n(CNS)_{6-n}]^-$ species in acetonitrile.

It is generally accepted that the thiocyanate ion will nitrogen-bond to a 'hard' metal such as niobium. Studies by Knox and Brown describing the preparation and characterization of $Nb(\underline{N}CS)_6^-$ [58,59] present infrared evidence indicating the presence of exclusive nitrogen-bonded thiocyanate in both solution (acetonitrile or 1,2-dichloroethane) and solid state. In 1968, Boland and co-workers reported the characterization of several six-coordinate niobium(V) species containing nitrogen-bonded thiocyanate ion[60,61]. These latter studies[60,61] cite uv spectral evidence to indicate that acetonitrile solutions incorporate a solvent molecule into the niobium primary coordination sphere, giving rise to $[NbCl_a(NCS)_b \cdot MeCN] \cdot cMeCN$ as well as $[Nb(NCS)_6]^- \cdot nMeCN$ species ($0 \leq a \leq 4$, $1 \leq b \leq 5$, $c \leq 1$). The latter study by Knox and Brown[59] demonstrated, through uv spectral and conductivity data, that the $Nb(NCS)_6^-$ ion is monomeric and molecular in acetonitrile at concent-

rations > 10^{-3} molar.

It was thought that a study of such complexes in solution by ^{93}Nb nmr might provide additional insight into the peculiarities of the niobium-thiocyanate system.

V.B.2 Results and Discussion

Redistribution reactions of niobium(V) with chloride and thiocyanate ligands in acetonitrile present a unique and complex problem that may best be studied by ^{93}Nb nmr. The problem is unique in that apparent random ambidentate behavior was observed for thiocyanate throughout an extensive range of redistribution products. Such extensive ambidentate behavior for thiocyanate had not previously been observed. The complexity of the problem derives from a statistical consideration of a three ligand (Cl, SCN, NCS) redistribution system and subsequent assignment of nmr observations within such statistical constraints. A limited case of a three ligand system ($[NbCl_nBr_{5-n}\cdot MeCN]$) has been encountered (Chapter V.A) and successfully interpreted through application of the Pairwise Rule. The present case comprises a considerably more difficult test for pairwise additivity, as will be observed.

The ^{93}Nb nmr spectra of niobium chloride-thiocyanate redistribution mixtures in acetonitrile indicated sixteen distinct resonance lines within a chemical shift range of 1342 ppm (Figure V, Table VI). Each resonance line was reasonably assigned to a distinct molecular niobium environment in absence of rapid ligand exchange, as the observed redistribution rates (≥ 1 hr. at 28°C) were slow compared to the nmr time scale.

Previous work[59] as well as present work (Chapter V.A and V.C) would strongly suggest the existence of solely molecular, monomeric, anionic* octahedral NbX_6^- species in such systems as will be described (Table VI). From this basis, one may readily ascertain that sulfur- as well as nitrogen-bonded thiocyanate must be present in the redistribution systems studied in order to account for the sixteen distinct magnetic environments experienced by the niobium nucleus.

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* No resonance corresponding to [$NbCl_5$·MeCN] (Chapter V.A) was observed, nor was expected.

FIGURE V

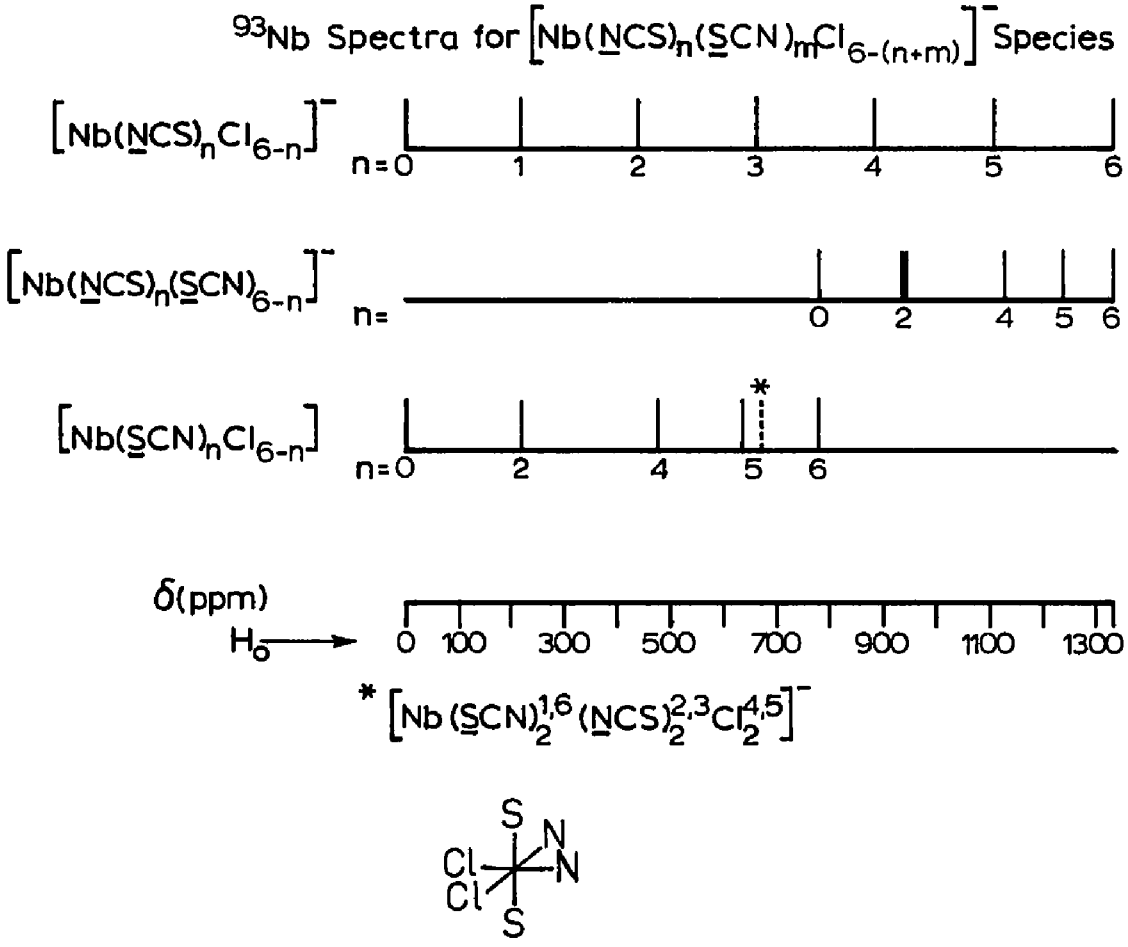
93Nb Spectra for [Nb(NCS)n(SCN)mCl6-(n+m)]- Species
[Nb(NCS)nCl6-n]-
n=0 1 2 3 4 5 6
[Nb(NCS)n(SCN)6-n]-
n= 0 2 4 5 6
[Nb(SCN)nCl6-n]
n=0 2 4 5 6
*
δ(ppm)
H0
0 100 300 500 700 900 1100 1300
* [Nb(SCN)2 1,6 (NCS)2 2,3 Cl2 4,5]-
S
N
Cl
N
Cl
S

TABLE VI

^{93}Nb Shifts for $[Nb(NCS)_n(SCN)_mCl_{(6-(n+m))}]^-$ Species in MeCN

Sample:	A	B	C	D	E	F	F'	G
δ ppm(*)	0 ss	-	-	0 ss	0 ss	0 ss	0 ss	0 ss
	-	220 mb	-	-	-	-	-	-
	233 mm	-	233 mm	230 mm	-	-	-	-
	-	457 mb	456 sm	461 wm	-	-	-	-
	475 mm	-	-	-	-	-	-	-
	-	615 ms	-	-	-	-	-	-
	633 sm	-	633 mm	630 sm	-	630 mm	-	-
	-	670 ss	-	-	-	-	-	-
	681 ms	-	680 vs,s	683 ms	-	-	-	-
	781 vss	781 ms	780 ms	780 vss	780 ms	780 vss	780 vss	-
	-	902 s,vb	902 m,vb	-	-	902 vs,m	-	-
	-	-	-	940 sm	940 sm	-	-	-
	947 mb	-	-	-	-	-	947 sm	-
	-	-	-	1117 sm	1115 sm	1120 sm	1120 mm	-
	1125 mb	1125 mb	1125 mb	-	-	-	-	-
	-	-	-	-	-	1235 mm	-	-
	1342 ws	1342 ms	1342 ms	1342 ss	1342 ss	1342 ms	1342 ws	1342 vss

Sample Composition:

A: $NbCl_5$ + nKSCN/MeCN
B: $KNb(NCS)_6$ + $NbCl_5$/MeCN
C: $KNb(NCS)_6$ + $NbCl_5$ + KCl/MeCn
D: As (C) with excess $NbCl_5$
E: $KNb(NCS)_6$ + Et_4NNbCl_6/MeCN
F: $Pb_4AsNb(NCS)_6$ + Et_4NNbCl_6/MeCN
F': As (F), 5 days at room temperature
G: As (F) in 1,2-dichloroethane

δ ppm(*)

Intensity
vs - very strong
s - strong
m - medium
w - weak

Linewidth
s - sharp
m - medium
b - broad

In acknowledging the existence of $[Nb(NCS)_n(SCN)_m Cl_{(6-(n+m))}]^-$ $(n+m \leq 6;\ 0 \leq n \leq 6)$ species, one is faced with an overwhelming number of possible stoichiometries and configurations. There are fifty-six (56) possible geometric configurations for the allowed twenty-eight (28) stoichiometries, of which twenty-seven (27) are for the eighteen (18) stoichiometries containing only two types of Cl, SCN and NCS ligands, and the remaining twenty-nine (29) for the ten (10) stoichiometries containing combinations of all three ligands (Table VIIB). Each configuration would cause rise of a single nmr resonance line. The problem was immediately reduced in that only sixteen resonance lines were observed. The goal was then to assign the observed resonances to species within the framework as outlined above.

The resonance at 0 ppm was due to the known reference species, $NbCl_6^-$. The resonance at 1342 ppm (Table VI) was the sole resonance observed in solutions reported to contain[58,59] $Nb(NCS)_6^-$. The resonance at 780* ppm was

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* Other observed shift values were substituted in the following analysis; however, no consistency could be obtained in subsequent data analyses.

assigned to $Nb(\underline{S}CN)_6^-$, an assignment based in part on the apparent nephelauxetic-niobium shielding dependence (Chapter V.D). In addition, this resonance had a line shape consistent with that anticipated for a symmetric ML_6 species. The validity of this assignment will be aptly demonstrated within the following analysis.

An approximation to the anticipated degree of magnetic shielding experienced by the niobium nucleus was obtained for all twenty-eight (28) possible stoichiometries on the assumption that there was a direct substituent-shielding correlation. This linear approximation (first-order) method and its results are summarized in Table VIIA. These calculated shift values obtained from the observed shift values assigned to $NbCl_6^-$, $Nb(SCN)_6^-$ and $Nb(NCS)_6^-$, (Table VIIA) were employed as an empirical aid to effect assignment of stoichiometries to observed resonances. As was the case with the $[NbCl_nBr_{6-n}]^-$ system (Chapter VA), a second-order substituent dependence of the chemical shift was observed. This dependence was satisfactorally accommodated by application of the Pairwise Additivity Rule (Chapter II). The presence of this second-order dependence enabled a distinction to be made among the various geometric isomers comprising a particular stoichiometry, consequently permitting assignment of configurations of stoichiometries

TABLE VIIA

Linear Approximation Shift Calculations for

$[Nb(NCS)_n(SCN)_mCl_{(6-n(n+m))}]^-$ Species (in ppm)

$(n+m \leq 6)$

SCN / NCS	m=0	1	2	3	4	5	6
n=0	0	130	260	390	520	650	780
1	224	354	484	614	744	874	-
2	447	577	707*	837	967	-	-
3	671	801	931	1061	-	-	-
4	895	1025	1155	-	-	-	-
5	1118	1248	-	-	-	-	-
6	1342	-	-	-	-	-	-

* eg. $\delta = 707$ ppm $= [Nb(NCS)_2(SCN)_2Cl_2]^-$

$$\delta_{calc} = \sum_{[6-(n+m)]=6} n\,\delta'_{NCS} + m\,\delta'_{SCN} + (6-(n+m))\,\delta'_{Cl^-}$$

$\delta' = 1/6\ \delta$ ppm $[NbX_6]^-$

$\delta'_{Cl} \simeq 0$

$\delta'_{NCS} = 224$

$\delta'_{SCN} = 130$

TABLE VIIB

$[Nb(NCS)_n(SCN)_mCl_{6-(n+n)}]^-$ Species; Available Configurations

NCS \ SCN	m=0	1	2	3	4	5	6
n=0	1 (1)	1	2 (1)*	2	2 (1)	1 (1)	1 (1)
1	1 (1)	2	3	3	2	1	
2	2 (1)	3	5 (1)	3	2 (2)		
3	2 (1)	3	3	2			
4	2 (1)	2	2 (1)				
5	1 (1)	1 (1)					
6	1 (1)						

* (1) indicates one configuration of stoichiometry $[Nb(SCN)_2Cl_4]^-$ observed.

to observed resonance lines.

Basically through a process of trial and error, all observed resonances were assigned to particular configurations. In this process, four 'classes' of shifts were considered; namely three groups containing only two of the ligands Cl, NCS and SCN, and a group containing all three ligand types. As resonances were assigned to species within each 'class', they were analyzed in accordance with the Pairwise Rule to determine configuration and to obtain pairwise interaction values to facilitate assignment of remaining resonances. This process resulted in the construction of the 'pairwise' matrix presented in Table VIII. Treatment of this entire matrix by multiple linear regression analysis produced solutions for the pairwise interaction parameters (η_{ij}) entirely consistent with those obtained through the above-mentioned partial analysis. The validity of the assignments (Table VIII) is attested to by the close correspondence of δ_{calc} and δ_{obs} values*.

Although calculated shift values are not presented for all 56 possible configurations, they may readily be determined by a summation of the products of the appropriate values of the interaction parameters (η_{ij}), each multiplied

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* All deviations, $|\delta_{calc}-\delta_{obs}|$, lie within the experimental error, expressed as a standard deviation.

TABLE VIII

Pairwise Additivity Assignments for $Nb(NCS)_n(SCN)_mCl_{(6-(n+m))}^-$ Species

Species	Additivity Coefficients						δ_{calc} $\Sigma c_{ij}\eta_{ij}$	δ_{obs} ppm
	Cl-Cl	S-S	N-N	Cl-S	Cl-N	S-N		
$NbCl_6$	12	0	0	0	0	0	2	0
$NbCl_5N$	8	0	0	0	4	0	230	232
$NbCl_4N_2$ cis	5	0	1	0	6	0	456	457
$NbCl_3N_3$ cis	3	0	3	0	6	0	679	681
$NbCl_2N_4$ cis	1	0	5	0	6	0	902	902
$NbClN_5$	0	0	8	0	4	0	1122	1118
NbN_6	0	0	12	0	0	0	1341	1342
NbS_6	0	12	0	0	0	0	782	780
NbS_4N_2* cis	0	5	1	0	0	6	946	947
NbS_4N_2 trans	0	4	0	0	0	8	939	940
NbS_2N_4 trans	0	0	4	0	0	8	1125	1126
$NbSN_5$	0	0	8	0	0	4	1234	1235
NbS_2Cl_4 trans	4	0	0	8	0	0	217	220
NbS_4Cl_2 trans	0	4	0	8	0	0	477	475
NbS_5Cl	0	8	0	4	0	0	630	633
$NbS_2^{1,6}N_2^{2,3}Cl_2^{4,5}$	1	0	1	4	2	4	674	670

* S = SCN
N = NCS

Additivity Parameter Values

$\eta_{Cl-Cl} \simeq 0$ ppm

$\eta_{\underline{S}CN-\underline{S}CN} = 65$

$\eta_{\underline{N}CS-\underline{N}CS} = 111.5$

$\eta_{Cl-\underline{S}CN} = 27$

$\eta_{\underline{S}CN-\underline{N}CS} = 85$

by the coefficient ($0 \leq c_{ij} \leq 12$) describing the particular configuration.

The following intervals (in ppm) separating geometric isomers of a particular stoichiometry were calculated:

stoichiometry	interval (ppm)
$[Nb(\underline{N}CS)_nCl_{6-n}]^-$ n = 2,3,4	3
$[Nb(\underline{S}CN)_n(\underline{N}CS)_{6-n}]^-$ n = 2,4	7
$[Nb(\underline{S}CN)_nCl_{6-n}]$ n = 2,4	11
$[Nb(\underline{S}CN)_n(\underline{N}CS)_mCl_{(6-(n+m))}]^-$ n ≥ 2	12

The best fit of calculated to observed shifts for $[Nb(\underline{N}CS)_nCl_{6-n}]^-$ species was indicative of the exclusive presence of cis-isomers (where n = 2,3,4). It should be noted, however, that the experimental error in this case is likely greater than the indicated 3 ppm interval separating cis-trans pairs. A reliable fit to the observed data is only obtained upon assignment of trans-configurations for those species containing $\underline{S}CN^-$ ligands. (The resonance at 947 ppm assigned to cis-$[Nb(SCN)_4(NCS)_2]^-$ is the sole exception.) The assignments given to the observed resonances indicate the following trends governing preferential configurations; (SCN trans to $\underline{S}CN$) > (SCN trans to $\underline{N}CS$) ≃ (SCN trans to Cl)

(NCS trans to Cl) > (NCS trans to NCS) ≃ (Cl trans to Cl)
Possibly, (SCN trans to SCN) ≃ (NCS trans to Cl).

It is of interest to note that resonances assigned to S-bonded thiocyanate species, particularly $Nb(SCN)_6^-$ at 780 ppm, only appear in the presence of chloride ion in acetonitrile solution. An acetonitrile solution of $Nb(NCS)_6^-$ produces the single sharp resonance at 1342 ppm and no resonances corresponding to $[Nb(NCS)_nSCN_{6-n}]^-$ ($0 \leq n \leq 6$) species upon prolonged standing. It is difficult to envisage the precise kinetic and thermochemical factors that dictate the ambidentate nature of the thiocyanate ion in these solutions.

No single solution (Table VI) contains all resonances reported. It would appear that resonances of these systems, and consequently species within these systems, are sensitive to the mode of preparation and relative concentrations of solutes. No particular pattern to explain these occurrences is immediately apparent.

Nonetheless, this system remains a prime demonstration of the ambidentate nature of thiocyanate.

V.C Additional Redistribution Products of the Type $[NbCl_nX_{6-n}]^-$, in Acetonitrile

V.C.1 Introduction

In a further attempt to establish the chemical shift pattern and range of the niobium nucleus, several redistribution products of $[NbCl_nX_{6-n}]^-$ (X = F, I, CN, N_3) were examined. This study was undertaken primarily to establish the chemical shifts for the various $[NbX_6]^-$ species; however, only NbF_6^- was observed directly. Resonance positions for $[Nb(N_3)_6]^-$ and $[NbI_6]^-$ were extrapolated by application of the Pairwise Additivity and Linear Approximation rules respectively.

V.C.2 The $[NbCl_nF_{6-n}]^-$ System

^{93}Nb resonances were observed for all seven allowed stoichiometries of the hexachlorofluoroniobates. Two redistribution solutions containing $Cs[NbF_6]$ or $NH_4[NbF_6]$ with $Et_4N[NbCl_6]$ in MeCN were studied. These two solutions did not produce identical chemical shift results (Table IX) and neither set of results was found to be linearly dependent upon halogen composition. Furthermore, neither chemical shift data set was found to bear a strict second-order (Pairwise Additivity) dependence. The relatively broad, diffuse resonance lines assigned to species

TABLE IX

^{93}Nb Shifts for $[NbCl_nF_{6-n}]^-$ Species in MeCN

	δ_{obs}* (ppm) Cs^+	δ_{calc} (ppm) first order	δ_{obs}* (ppm) NH_4^+
$[NbCl_6]^-$	0	0	0
$[NbCl_5F]^-$	268	259	258
$[NbCl_4F_2]^-$	524	519	491
$[NbCl_3F_3]^-$	824	778	805
$[NbCl_2F_4]^-$	1093	1037	1077
$[NbClF_5]^-$	1340	1297	1327
$[NbF_6]^-$	1556	1556	1558

* Standard deviation of result due to calibration uncertainty in 3 ppm.

$[NbCl_nF_{6-n}]^-$ where $1 \leq n \leq 5$ may be indicative of Nb-F coupling or some mode of rapid chemical exchange of the ligands. However, it may be noted that in all cases the Nb-F coupling in $[NbF_6]^-$ was always resolved and no broadening of the $[NbCl_6]^-$ resonance was observed. Insufficient data were available to effect further interpretation of this system.

V.C.3 $[NbCl_5I]^-$ in Acetonitrile

Attempts were made to observe resonances for a variety of anionic hexahaloniobates containing iodine with either chlorine or bromine in acetonitrile solution. With the exception of the resonance at -365 ppm assigned to $[NbCl_5I]^-$, no unique resonances were detected. In each solution studied, the predominant or sole resonance was that of $[NbCl_6]^-$ or $[NbBr_6]^-$. Presumably these observations indicate the low solubility of iodide containing species and the consequent directing of the position of the redistribution equilibria to favour the more soluble species, namely the hexachlorides and bromides.

On the basis of the Linear Approximation method, the resonance at -365 ppm assigned to $[NbCl_5I]^-$ can be extrapolated to give a chemical shift value for $[NbI_6]^-$ of -2190 ppm.

V.C.4 The $[NbCl_n(N_3)_{6-n}]^-$ System

Addition of azide ion ($(N_3)^-$) to $NbCl_5$ in MeCN produced, upon standing, an orange solution. Four ^{93}Nb resonances were observed in this solution (Table X) and were assigned as $[NbCl_n(N_3)_{6-n}]^-$ species where $3 \leq n \leq 6$. Analysis of the chemical shift data by the Pairwise Additivity Rule indicated the presence of trans-isomers where n = 4,3; (N_3 trans N_3 > N_3 trans Cl). The extraction of the interaction parameter, $\eta_{N_3-N_3}$, allows prediction of the chemical shift of the unobserved $[Nb(N_3)_6]^-$ species as 896 ppm.

V.C.5 The $[NbCl_n(CN)_{6-n}]^-$ System

Mixtures of cyanide ion and $NbCl_5$ in MeCN produced two to three discernable sharp and closely spaced ^{93}Nb resonances in the region 0-100 ppm. The resolution of these resonances was insufficient to extract chemical shift data; however, on the basis of the observed pattern an approximation to the resonance position of the $[Nb(CN]_6]^-$ species is suggested to be ca. 150 ppm.

TABLE X

^{93}Nb Shifts for $[NbCl_n(N_3)_{6-n}]^-$ Species in MeCN

Species		Additivity Coefficients η_{Cl-Cl}	η_{Cl-N_3}	$\eta_{N_3-N_3}$	δ_{calc} $\Sigma C_{ij}\eta_{ij}$	δ_{obs} ppm (±3)
$NbCl_6^-$		12	0	0	-1.5	0
$[NbCl_5(N_3)]^-$		8	4	0	167	164
$[NbCl_4(N_3)_2]^-$	cis	5	6	1	328	337
	trans	4	8	0	335	
$[NbCl_3(N_3)_3]^-$	cis	3	6	3	477	485
	trans	2	8	2	485	
$[Nb(N_3)_6]^-$		0	0	12	896	*

Additivity Parameter Values (ppm)

$$\eta_{Cl-Cl} \simeq 0$$

$$\eta_{Cl-N_3} = 42.1$$

$$\eta_{N_3-N_3} = 74.8$$

* not observed

V.D The Anomalous Nuclear Shielding of Niobium in $[NbX_6]^-$ Species

Observed or calculated resonance positions for eight $[NbX_6]^-$ species in MeCN are tabulated in decreasing order of chemical shifts (Table XI). Arranged in this fashion, the entire series bears a striking resemblance to the nephelauxetic series:

TABLE XI

^{93}Nb Shifts for $[NbX_6]^-$ Species

$[NbX_6]^-$ Species X^- =	δ (ppm)
F	1556
NCS	1342
N_3	900*
SCN	780
CN	150**
Cl	0
Br	-731
I	-2190*

* calculated

** approximation

It is generally assumed that the paramagnetic term of the chemical shift expression dominates the observed shift range of any heavy nucleus. There are only two factors in the paramagnetic expression as written which could appreciably

$$\sigma_p = - \frac{C[L(L+1)]}{\Delta E \langle r^3 \rangle}$$

influence the magnitude and direction of the chemical shift phenomenon, these being the average energy, ΔE, and the mean value of r^{-3}, $\langle r^{-3} \rangle$. The latter term is proportional to the cube of the effective nuclear charge, a factor generally assumed to vary as the nephelauxetic[7] series. Obviously, either or both of these terms could control the observed shift range. These effects will be considered separately.

(a) The ΔE Dependence

The average energy, ΔE, of a molecular system has generally been discussed in terms of the lowest lying electronic transition. This point has been discussed in Chapter IV with regard to the direction of nuclear shielding. Typical metal tetrahalides of T_d symmetry exhibit the following trend of lowest lying electronic transitions with regard to halogen composition:

$$I < Br < Cl$$

this also being the direction of anticipated nuclear shielding if ΔE^{-1} is dominant in σ_p.

As this is the ordering observed for the chemical shifts of NbX_6^- species (as well as TiX_4 species), the following data were assembled (Table XII) for comparative purposes. A rational trend between δ ppm and ΔE^{-1} may be indicated for the TiX_4 species, although a reversed order is indicated for Ge and Sn species. However, in the more complete niobium series, no such trend is apparent.

(b) The $\langle r^{-3} \rangle$ Dependence

The nephelauxetic series, in part, is reproduced below. This series is arranged in order of increasing ability of ligands to cause d-orbital or 'cloud' expansion, a factor which simultaneously increases the effective nuclear charge

$$F^- < NH_3 < \underline{N}CS^- < Cl^- \sim CN^- < Br^- < I^-$$

Were the nephelauxetic effect equated to the possible $\langle r^{-3} \rangle$ dominance of σ_p and therefore, the observed shifts of niobium, the order of increased nuclear shielding should follow the above series as written. In actual fact, the series ordering is retained, albeit with a complete reversal of direction.

TABLE XII

Select Chemical Shift and Charge Transfer Data

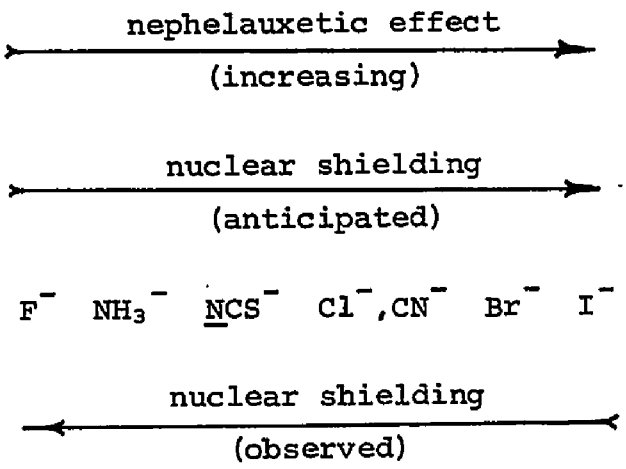
Species	Color (solution)	ΔE[a] (kK)	δ ppm
$TiCl_4$	colorless	34.8 [b]	0
$TiBr_4$	lt. orange	28.7 [b]	-500
TiI_4	deep red	19.4 [b]	n.a.
$GeCl_4$	colorless	> 50 [b]	0
$GeBr_4$	lt. orange	> 50 [b]	343
GeI_4	red-orange	27.8 [b]	1117
$SnCl_4$	colorless	48.4 [b]	0 [d]
$SnBr_4$	lt. orange	41.6 [b]	485 [d]
SnI_4	orange	27.4 [b]	1550 [d]
NbF_6^-	colorless	-	1556
$Nb(NCS)_6^-$	deep-red	-	1342
$Nb(N_3)_6^-$	orange	-	900
$Nb(SCN)_6^-$	red	-	780
$NbCl_6^-$	yellow	27 [c]	0
$NbCl_5Br^-$	lt. orange	25 [c]	-132
$NbCl_5I^-$	brown-black	15 [c]	-365
$NbBr_5Cl^-$	brown-red	16 [c]	-621
$NbBr_6^-$	red-maroon	21 [c]	-731
$NbBr_5I^-$	dark-brown	20 [c]	~ -980
NbI_6	black	-	~-2200

[a] ΔE taken as the lowest energy charge transfer band

[b] ref. 35

[c] ref. 46, 51

[d] ref. 17



It is likely of little more than passing interest that the niobium shifts vary as the inverse of the nephelauxetic effect, for the latter may not be applicable to d^0 systems. Similarly, the apparent lack of correlation between ΔE^{-1} and the observed shifts may not be entirely catastrophic, for is ΔE actually typified by the lowest lying electronic transition? Future studies may reveal that trends of σ, π-donor and acceptor properties of ligands may provide a superior probe in the development of an understanding of the modes of nuclear shielding.

CHAPTER VI

ANTIMONY-121 NMR STUDY OF HEXACHLOROBROMOANTIOMONATES

VI.1 Introduction

The existence of hexachlorobromoantimonates has been doubted in past reviews[62,63]. The reaction of $SbCl_4^+$ and Br^- ions under appropriate conditions is reported[64] to lead to mixtures of the hexachloro- and hexabromoantimonates, separated by fractional crystallization and identified through x-ray powder analysis of the tetraethylammonium salts. In addition it has been suggested on the basis of ultraviolet spectra, that acetonitrile solutions of $SbBr_6^-$ decompose to $SbBr_3 \cdot Br_3^-$ [64].

A recent study[65] has reported conclusive evidence regarding the preparation and characterization of the $[SbCl_5Br]^-$ ion. Laser Raman and differential scanning calorimetry evidence is cited[65] to distinguish the $[SbCl_5Br]^-$ ion from a fortuitous 5:1 (mole) mixture of $[SbCl_6]^-$ and $[SbBr_6]^-$. In addition, a recent single crystal x-ray analysis has characterized Et_4NSbBr_6 as a symmetric octahedral Sb(V) species[66].

These factors would appear to indicate a reasonable degree of stability for chlorobromoantimonates and would further suggest that solubility (kinetic), and not thermochemical factors dictate the nature of species separated from solution. It becomes obvious from previous reports[64] that all seven possible stoichiometries of $[SbCl_nBr_{6-n}]^-$ must exist in solution, even if only in a transient state, for reaction of $SbCl_4^+$ and Br^- to yield $[SbCl_6]^-$ and $[SbBr_6]^-$.

The purpose of this investigation was to determine the nature of $[SbCl_nBr_{6-n}]^-$ species in acetonitrile solution via ^{121}Sb nmr.

VI.2 Results and Discussion

Of the samples studied (see experimental), identical chemical shifts were obtained for corresponding stoichiometries, regardless of the method of preparation or the cation employed. Solubility was the limiting factor in these studies, the higher chlorides being more soluble than the bromides. In only the Et_4NSbCl_6: Et_4NSbBr_6 (1:1 mole ratio) sample were all seven resonances corresponding to the possible stoichiometries observed simultaneously.

The rates of halogen exchange were generally very slow. The complete redistribution between Et_4NSbCl_6:Et_4NSbBr_6 in acetonitrile required $\sim$ 80 hours at 28°C. Addition of

bromide ion to Et_4NSbCl_6 required ~ 20 hours (28°C) to produce resonances corresponding to $Et_4N[SbCl_nBr_{6-n}]$ with n = 6,5,4, and 3. In the latter case, the solution exhibited a color change from near-colorless to light orange during this time period, further indicating the formation of mixed species. ($[SbCl_6]^-$/MeCN is colorless to very pale yellow; $[SbBr_6]^-$/MeCN is a deep orange-red.) The redistribution of halogen species would appear to be random in nature, although low solubility prevents accurate verification of this.

Obviously, stoichiometric halogen exchange rates are sufficiently slow such that they are not expected to contribute to either line width or position. However, the relatively low solubility of the higher bromide species required the use of high power levels such that resonance lines were artificially broadened. Under the instrumental conditions employed, the broadest resonances for $[SbCl_nBr_{6-n}]^-$ species were observed where n = 1,2,4,5 while the resonances where n = 0,3,6 were relatively sharp ($\nu_{\frac{1}{2}} \simeq 350$ Hz). A similar trend was observed for the analogous niobium species. It should be mentioned that no resonances were detected for samples containing Sb(III) species.

In the complete redistribution series $[SbCl_nBr_{6-n}]^-$ $0 \leq n \leq 6$, the ^{121}Sb nucleus may experience a maximum of

ten magnetically non-equivalent environments. Four of these will correspond to the stoichiometries where n = 0,1,5, 6 and the remaining six will correspond to the three cis-trans pairs of stoichiometries n = 2,3,4.

In the present case, seven distinct antimony resonances were observed and were positioned such that they corresponded to the seven allowed stoichiometries. The question then arises as to the configurations of species where n = 2,3,4. The following factors must be considered in deriving a solution to this problem.

(i) accidental degeneracy resulting in two different isomers having the same chemical shift,

(ii) a kinetic isomerization process occurring rapidly on the nmr time scale giving rise to a single averaged signal for both cis and trans isomers,

(iii) certain isomers being thermodynamically more stable than others such that not all six isomers from the three geometric pairs exist in detectable concentrations in solution.

The available data and consequent discussion of these factors are identical to that presented for the $[NbCl_nBr_{6-n}]^-$ system (Chapter V, pg. 40), concluding that factor (iii) is in operation.

TABLE XIII

^{121}Sb Shifts for $[SbCl_nBr_{6-n}]^-$ Species in MeCN

Species		Additivity Coefficients η_{Cl-Cl}	η_{Cl-Br}	η_{Br-Br}	δ_{calc} $\Sigma C_{ij}\eta_{ij}$	δ_{obs}* ppm (±5)	δ_{calc} First Order
$SbCl_6^-$		12	0	0	-1.4	0	0
$SbCl_5Br^-$		8	4	0	383	380	405
$SbCl_4Br_2^-$	cis	5	6	1	778	780	810
	trans	4	8	0	767		
$SbCl_3Br_3^-$	cis	3	6	3	1183	1180	1215
	trans	2	8	2	1172		
$SbCl_2Br_4^-$	cis	1	6	5	1588	1590	1620
	trans	0	8	4	1578		
$SbClBr_5^-$		0	4	8	2004	2005	2025
$SbBr_6^-$		0	0	12	2431	2430	2430

Additivity Parameter Values

$$\eta_{Cl-Cl} \simeq 0 \quad \text{ppm}$$

$$\eta_{Cl-Br} = 96.0$$

$$\eta_{Br-Br} = 202.7$$

Working on this basis, application of the Pairwise Additivity Model to the observed chemical shift data produced calculated shift values (Table XIII) indicating the presence of cis-isomers to the virtual exclusion of trans-isomers in solution.

This preference for cis configurations displayed by this system is again identical to that displayed by the niobium system. Consequently, the discussion regarding the cis preference for the $[SbCl_nBr_{6-n}]^-$ system is identical to that presented for the $[NbCl_nBr_{6-n}]^-$ system in Chapter V, pg. 47.

Although there are many points of close correspondence between the analogous antimony and niobium chloride-bromide systems, as determined in part by their nmr spectra, it must again be noted that Nb(V)d^0 (as Ti(IV)d^0) exhibits the anomalous order of nuclear shielding (as compared to Sb(V) and Ge(IV)). As with the tetrahedral species of germanium and titanium, the similarity in the chemistry of the octahedral halide systems of niobium and antimony leaves one perplexed as to the nature of this shielding phenomenon.

CHAPTER VII

SUMMARY

The study of the chemical shift phenomenon has been of central importance in this study. With the advent of ^{13}C Fourier Transform nmr studies in very recent years, the chemical shift phenomenon has been gaining acceptance as a tool of scientific investigation capable of meaningful interpretation rather than being a parameter of mere chemical novelty. The chemical shift emphasis is, in part, of necessity when considering systems of nuclear spin, $I > \frac{1}{2}$, for spin-spin couplings (being of prime importance in ^{1}H and ^{19}F studies) are rarely observed in such systems.

In addition to possessing $I > \frac{1}{2}$, the nuclei examined in this study are exclusively the central atoms in either four or six-coordinate species such that linewidths as well as shift values, should be indicative of ligand configuration about the core atom through interaction of the nuclear quadrupole with any existing field gradients. Spectrometer limitations negated any useful linewidth studies.

The present study has interpreted chemical shift data to achieve several ends, as summarized below:

$^{73}GeX_4$
- a demonstration of the periodicity of the chemical shift range
- a simplification of the available Raman data
- ability to conveniently perform kinetic studies.

$^{47,49}TiX_4$
- a simplification of the available Raman data concerning the state of association of liquid $TiCl_4$
- the first evidence of anomalous nuclear shielding
- a potential means of deriving kinetic data

^{93}Nb
- direct determination of structural evidence through extension and application of 'Pairwise Additivity'
- the transferability of interaction parameter (η) values among anionic and neutral octahedral species
- additional evidence for anomalous nuclear shielding, a phenomenon peculiar to d^0 systems to date
- potential collection of kinetic data

- ability to characterize redistribution systems, with regard to stoichiometries and configurations of products, that would be difficult or impossible to analyze through other spectroscopic techniques (such as Raman).

^{121}Sb

- direct determination of structural evidence through application of 'Pairwise Additivity'
- potential collection of kinetic data
- successful completion of a study which, in all probability, would be impossible by other spectroscopic techniques
- evidence offered for the existence of species thought by some not to exist

The anomalous shielding experienced by the d^0 metals, Ti(IV) and Nb(V), has been noted but no complete explanation of this phenomenon can be offered at this time.

Although nmr studies as reported here are limited to diamagnetic systems, the large number of nmr sensitive nuclei and the current generation of 'state-of-the-art' spectrometers could allow expansion of nmr as a useful probe into many new areas of chemistry as well as further studies involving chemical systems of the nuclei presented here.

CHAPTER VIII

EXPERIMENTAL

VIII.A The NMR Spectrometer and Spectroscopic Techniques

Spectra were obtained using a Varian 4200 B wide-line spectrometer with a V-4210 A variable-frequency oscillator (2-16 MHz) and a V-3400 9-inch magnet with Fieldial stabilization and sweep capability. The magnet pole caps were modified to give a homogenity better than 60 milligauss (~ 4 ppm at 14.1 KG) over the 15 mm. o.d. sample tubes used in this study. Resonance lines were recorded under slow passage conditions as derivatives of dispersion signals, and calibration was effected by the generation of audio-frequency sidebands. Chemical shift values, designated by δ, are quoted in parts per million (ppm) with positive shifts denoting increased shielding. Reported chemical shifts represent the average values obtained by sweeping the magnetic field at least five times in both increasing and decreasing directions. The quoted precision of the chemical shifts (as standard deviations) takes account of the calibration uncertainty as determined by multiple measurements of the shift. No distinction

TABLE XIV

Nuclear Spins, Moments and Magnetic Resonance Frequencies[30]

Isotope Z	El	A	Spin I	NMR Frequency (MHz) for X KGauss Field		Natural Abundance (%)	Relative Sensitivity to $^1H_1$ for equal numbers of nuclei ($dH/dt = 0$)	Magnetic Moment ($u = X$ eh/4πMc)	Electric Quadrupole Moment Q (in 10^{-24} cm^2-barns)
				10	14.1				
32	Ge	73	9/2	1.485	2.094	7.76	1.4×10^{-3}	-0.87	-0.2
22	Ti	47	5/2	2.4000	3.304	7.28	2.09×10^{-3}	-0.79	-
22	Ti	49	7/2	2.40051	3.385	5.51	3.76×10^{-3}	-1.10	-
41	Nb	93	9/2	10.407	14.674	100	0.482	6.14	-0.2
51	Sb	121	5/2	10.189	14.366	57.25	0.160	3.34	-0.5
51	Sb	123	7/2	5.518	7.780	42.75	4.6×10^{-2}	2.53	-0.7

could be made between the resonance position of any particular reference species used either as an internal or external standard.

The nuclear properties of the elements studied are summarized in Table XIV.

VIII.B Sample Preparation and Study

VIII.B.1 Germanium-73

Germanium-73 nmr spectra were observed with difficulty, at 2.09 MHz. The ^{73}Ge isotope is unique among the main group elements of Group IV in that, with nuclear spin I = 9/2, it is the only nmr active isotope with $I > \frac{1}{2}$. Consequently, ^{73}Ge possesses a nuclear electric quadrupole moment that will interact with any electric field gradient generated by the bonded atoms such that resonance lines will tend to be broad for any species of less than cubic symmetry. The poor detection properties of ^{73}Ge (Table XIV), coupled with the inherent breadth of the lines, restrict detection of resonance signals to relatively concentrated solutions ($\geq$ 1 molar). In the study of halogen redistribution products, the lowered concentration of each species necessitated the use of increased power levels and higher modulation frequencies to produce a signal-to-noise ratio adequate for obtaining chemical shift information. Under these circum-

stances, accurate linewidth measurements for the mixed tetrahalides were precluded.

Linewidths of 25 Hz were observed for samples of the neat tetrahalides, a value which represents the homogeneity limit of the magnet used in the study. By analogy with ^{27}Al resonances in AlX_4^- species[13,68], the natural linewidth for ^{73}Ge in a halogen environment having Td symmetry is probably considerably less than 25 Hz. All observed resonance lines assigned to mixed tetrahalogermanes were split by 80 Hz modulation, and the majority were split by 40 Hz modulation. This strongly suggests that natural linewidths of observed resonances are < 80 Hz.

Sample Preparation. The germanium tetrahalides were obtained as "ultra-pure" grade from Alfa Inorganics. Further purification of these samples did not alter the resonance lines or redistribution rates. Carbon disulfide was distilled and stored over Linde 3A molecular seive. Samples were prepared in 15 mm o.d. nmr tubes under anhydrous conditions by employing standard vacuum line and dry box techniques. $GeCl_4$ and $GeBr_4$ were studied as neat liquids and in carbon disulfide solution, while GeI_4 was studied as a saturated solution in carbon disulfide. The three 1:1 mole ratio samples involving two different halogens and the 1:1:1 mole ratio sample involving all three halogens were

prepared from the parent tetrahalides. In each case, 5 millimole samples of each tetrahalide were mixed, and carbon disulfide was added where necessary to bring GeI_4 into solution. Carbon disulfide did not alter the resonance positions of either $GeCl_4$ or $GeBr_4$.

VIII.B.2 Titanium-47,49

Titanium-47,49 nmr spectra were observed at 3.38 MHz, again with some difficulty as the values of the nmr detection parameters (Table XIV) are rather unfavourable. Nonetheless, intense resonances of high signal-to-noise ratio were observed for the neat tetrahalides (Figure II). The unique proximity of the resonance frequencies of ^{47}Ti and ^{49}Ti was used to advantage. The shift between the two isotopes of neat $TiCl_4$ was accurately measured at 271 (± 3) ppm. Thereafter, all spectra were calibrated using the ^{47}Ti-^{49}Ti isotope shift. The half-height line width for each isotope under the resonance conditions normally employed was about 50 Hz for both $TiCl_4$ and $TiBr_4$. Further examination of each of these four resonance lines revealed splitting by a 40 Hz sweep frequency and no splitting by a 20 Hz sweep frequency. This indicates that the natural line width approaches the limits of magnetic field homogeneity (about 25 Hz). Also, with the use of sweep frequencies less than 40 Hz, the signals were barely detectable. Thus useful

line width measurements were precluded.

Sample Preparation. The titanium(IV) tetrahalides were obtained from Alfa Inorganics and, except for TiI_4, were normally used without further purification. A sample of $TiCl_4$ purified by distillation in a tapless vacuum line showed no detectable change in signal position or width compared to an unpurified sample. Since titanium(IV) tetraiodide is particularly susceptible to hydrolysis, it was purified by repeated vacuum distillation in a tapless apparatus. Spectroscopic grade cyclohexane and carbon tetrachloride were dried by standing over molecular sieves.

All sample handling operations involving $TiCl_4$, $TiBr_4$ and TiI_4 were carried out under a dry nitrogen atmosphere.

The $^{47,49}Ti$ nmr spectrum of titanium(IV) tetrabromide was obtained from a sample warmed to a little above its melting point (39^{o}). All other samples were studied at room temperature.

Resonances Not Found. $^{47,49}Ti$ resonances were not detected for solid $TiBr_4$ or solid TiI_4. Solutions of TiI_4 in cyclohexane, carbon tetrachloride and carbon disulphide gave no observable signals, presumably due to the low solubility of TiI_4 in these solvents. No signals were detected for $TiCl_4$ in conc. HCl, $TiBr_4$ in conc. HBr,

$((C_2H_5)_4N)_2TiCl_6$ in acetonitrile, TiF_4 in trifluoroacetic acid and TiF_4 in acetonitrile. Low solubility may well be responsible for the absence of detectable signals in the latter three solutions.

VIII.B.3 Niobium-93

Niobium-93 nmr spectra were obtained at 14.67 MHz. Niobium-93 presents itself as a most favourable nucleus for nmr investigation, possessing 100% abundance, high detection sensitivity and a small electric quadrupole moment (Table XIV). The latter quantity implies that resonance lines of narrow to medium width are obtainable for six-coordinate species of less than O_h symmetry, as was found to be the case. In addition, the niobium compounds studied herein are moderately soluble in acetonitrile (0.5 - 1.5 molar) such that spectra of good quality are readily obtainable. As was the case with all nuclei studied here, all observed resonance line positions were insensitive to dilution and slight temperature changes, implying that in all cases, molecular species were being observed. Spectra calibration was effected by the generation of audio-frequency side bands (ca. 1000-1500 Hz) on the $[NbCl_6]^-$ resonance.

Little difficulty was encountered in the preparation and manipulation of the niobium(V) compounds employed in this study, provided that the absence of water and oxygen was strictly enforced. Consequently, all sample manipulation was performed under a dry nitrogen atmosphere (glove bag or dry-box) or by standard vacuum line techniques.

Solvents (MeCN, CH_2Cl_2 and 1,2-dichloroethane) were rigourously dried by prolonged reflux over, and fractional distillation from calcium hydride while under a dry nitrogen atmosphere. High purity niobium pentachloride, pentabromide and pentafluoride were used as received from Alfa Inorganics. Tetraethylammonium chloride and bromide as well as all appropriate potassium halides and pseudo-halides were dried by standard techniques. Tetraethylammonium niobium hexachloride and hexabromide were prepared as described previously[46,48-50] in the appropriate redistilled thionyl halide. Similarly, $NbOCl_3$ [67] and $MNb(NCS)_6$ [58,59] were prepared by literature methods. The NbF_6^- species was prepared either by

$$NbF_5 + \tfrac{1}{2}(NH_4)_2CO_3 \xrightarrow[48\%\ aq.]{HF} NH_4[NbF_6]$$

$$NbF_5 + CsF \xrightarrow[48\%\ aq.]{HF} CsNbF_6$$

or in situ

$$NbF_5 + NH_4F \xrightarrow{MeCN} [NbF_6]^- + NH_4^+$$

Within the limits of spectroscopic detection (of niobium resonances), varying total niobium concentration was observed to have no effect on the resultant spectra with regard to line shape or position. Similarly, varying the mole ratio of the reagents in all samples of redistribution systems had no discernable effect on the spectra other than an enhancement of the intensities of certain lines at the expense of others. Consequently, the equilibrium position of such redistribution systems could be altered within limits such that each resonance line could be studied in detail.

$[NbCl_nBr_{6-n}]^-$ Solutions. The following solutions were prepared in dry acetonitrile:

$Et_4N[NbCl_6] + Et_4N[NbBr_6]$

$Et_4N[NbCl_6] + NbBr_5 + KBr$

$Et_4N[NbCl_6]$ + excess KBr

$NbCl_5$ + excess KBr

$NbBr_5$ + excess KCl

$NbCl_5$ + excess Et_4NBr

$NbCl_5 + KCl + NbBr_5 + KBr.$

All of these solutions gave rise to similar seven-line ^{93}Nb spectra. The resonance positions and lineshapes were found to be independent of the cation present and of the Cl:Br:Nb

ratio as expected for a random redistribution of halogens among $[NbCl_nBr_{6-n}]^-$ species. Total niobium concentration was generally in the range of 0.5 to 1 molar.

$[NbCl_nBr_{5-n}\cdot MeCN]$ Solutions. The following solutions were prepared in dry acetonitrile, dichloromethane, or 50 mole % mixture of the two solvents.

Solute	Solvents
$[NbX_5\cdot MeCN]$	MeCN; CH_2Cl_2
Nb_2X_{10}	MeCN; 50 mole% $MeCN/CH_2Cl_2$
Nb_2X_{10} + 2MeCN	CH_2Cl_2
Nb_2Cl_{10} + Nb_2Br_{10}	MeCN; 50 mole% $MeCN/CH_2Cl_2$
Nb_2Cl_{10} + Nb_2Br_{10} + 4MeCN	CH_2Cl_2

(X = Cl,Br)

Identical resonance shapes and positions were observed for each assigned species within the same solvents. A systematic solvent dependence of the chemical shift, forcing to lower field, was observed upon changing from MeCN to 50 mole % $MeCN/CH_2Cl_2$ to CH_2Cl_2. Total niobium concentration was generally in the vicinity of 1.5 M.

$[Nb(SCN)_n(NCS)_mCl_{6-(n+m)}]^-$ Solutions. Eight solutions, the components of which are described in Table VI, pg.53, were prepared for study. All samples were prepared as concentrated or

saturated solutions (0.5 - 1 molar in niobium). The Cl:SCN:Nb ratio was generally 3:3:1, although it was varied from 5:1:1 to 1:5:1 in an attempt to detect additional resonance lines. All redistribution solutions, which were deep red in colour, required one to several hours to attain final equilibrium at room temperature. Redistribution did not occur in 1,2-dichloroethane, although this was likely a function of the low dielectric constant of this solvent. Resonance positions were independent of solution temperature.

$[NbCl_nX_{6-n}]^-$ Solutions. All solutions herein were prepared in acetonitrile, and niobium concentration was in the vicinity of 0.5 - 1 molar. In the case where X = F, the Cl:F:Nb ratio was 3:3:1. Species of $[NbCl_nX_{6-n}]^-$ (X = N_3, CN, I) were observed by addition of excess KX to MeCN solutions of $Et_4N[NbCl_6]$ or Nb_2Cl_{10}.

Potential Impurities. Because of the high affinity of niobium for oxygen, it is possible that oxyhaloniobates could arise as impurities in the solutions under study. The ^{93}Nb spectra for these potential impurities in MeCN solution were obtained by preparing $NbOCl_3$ according to the published procedure[67], and then adding excess chloride ion to this solution to obtain the higher chlorides. A similar procedure was used for the oxybromoniobates, except in this

case the pure $NbOBr_3$ was not isolated. The ^{93}Nb spectra observed for these species were as follows:

Solute in MeCN	^{93}Nb shift, ppm	Linewidth, Hz
$NbOCl_3$	503	700
$[NbOCl_{3+n}]^{n-}$ $(n \simeq 2)$	482	200
$[NbOBr_{3+n}]^{n-}$ $(n \simeq 2)$	200	200

No resonance lines having these characteristics were observed in any of the other systems studied.

VIII.B.4 Antimony-121

Antimony-121 spectra were obtained at 14.37 MHz. The ^{121}Sb isotope, rather than ^{123}Sb, was employed as the nmr probe into the antimony species studied due to the higher detection sensitivity of the former (Table XIV).

In essence, the preparation and manipulation of $[SbCl_nBr_{6-n}]^-$ species were similar to those employed for analogous $[NbCl_nBr_{6-n}]^-$ species. Anhydrous conditions were enforced. High purity compounds, $SbCl_5$, $SbCl_3$ and $SbBr_3$ were used as received from Alfa Inorganics. Tetraethylammonium and potassium chlorides and bromides were dried by standard techniques, and acetonitrile was dried as before over CaH_2. The species Et_4NSbCl_6 was prepared as the analogous niobium salt[46,48] from $SbCl_5$ and Et_4NCl in thionyl chloride. Et_4NSbBr_6 was prepared by the method of

Lawton[69] with slight modifications.

$$SbBr_3 + Et_4NBr + Br_2 \xrightarrow{MeCN} Et_4NSbBr_6$$

As with the analogous niobium compounds, resonance shape and position were found to be independent of total antimony concentration and, or Cl:Br:Sb ratio. Therefore, the total antimony concentration (~ 0.5 molar) and the Cl:Br:Sb ratio employed were those which produced the better spectra. All samples were prepared in MeCN.

$[SbCl_nBr_{6-n}]^-$ (Sb(V)) Samples in MeCN

Et_4NSbX_6	X = Cl or Br
$nEt_4NSbCl_6 + (6-n)Et_4NSbBr_6$	$(1 \leq n \leq 5)$
$Et_4NSbCl_6 + n$ KBr (or Et_4NBr)	$(1 \leq n < 10)$
$Et_4NSbBr_6 + n$ KCl (or Et_4NBr)	$(1 \leq n < 6)$

Sb(III) Samples* in MeCN

SbX_3	X = Cl or Br
$SbCl_3 + n\ Et_4NCl$	n = 1,3, > 3
**$SbBr_3 + n\ Et_4NBr$	n = 1,3, > 3

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* no ^{121}Sb resonances were detected for any Sb(III) species

** Addition of Br_2 to this solution (n = 1) oxidized Sb(III) to Sb(V) → $SbBr_6^-$ resonance.

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